United States Patent [19]

Polaroid Corporation et al.

[11] **3,816,125**

[45] **June 11, 1974**

[54] **PHOTOGRAPHIC PRODUCTS AND PROCESSES**

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[52] **U.S. Cl.** .... **96/3,** 96/29 D, 96/77, 96/99, 96/100

[51] **Int. Cl.** **G03c 7/00,** G03c 5/54, G03c 1/40, G03c 1/10

[58] **Field of Search** .... 96/3, 29 D, 77, 76 R, 95, 96/114.1

[56] **References Cited**

UNITED STATES PATENTS

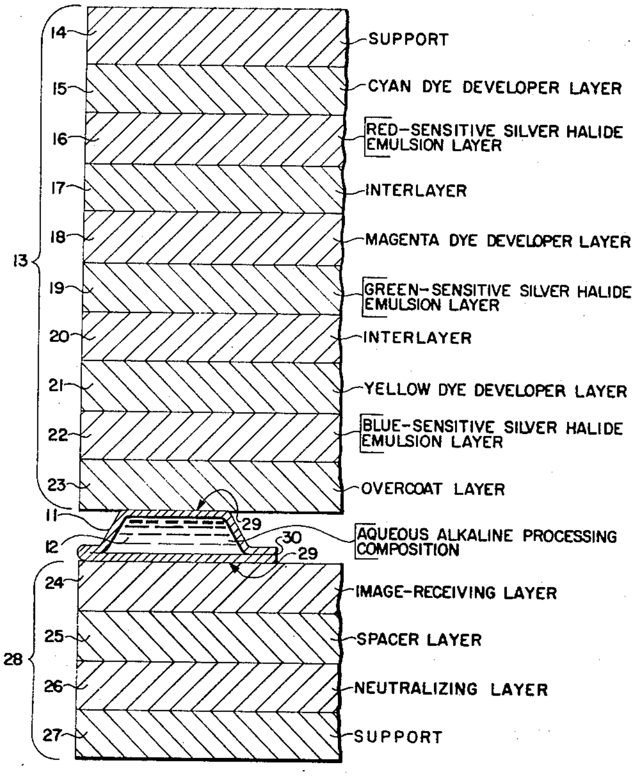
3,173,786	3/1965	Green et al.	96/3
3,649,265	3/1972	Stewart	96/3
3,698,896	10/1972	Abbott	96/3

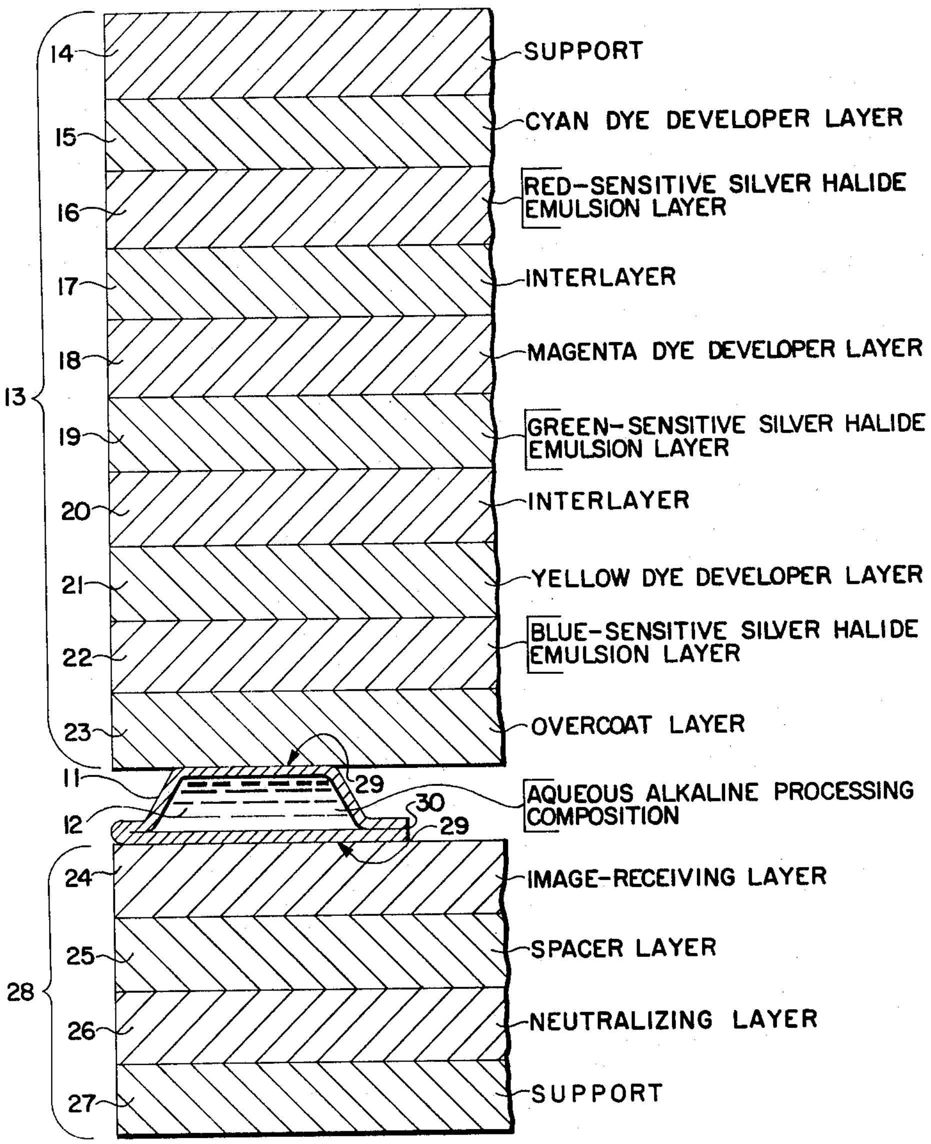
Primary Examiner—Norman G. Torchin
Assistant Examiner—Richard L. Schilling

[57] **ABSTRACT**

The present invention is directed to photography and particularly to diffusion transfer color processes wherein the color separation and highlights are significantly enhanced by carrying out said process in the presence of an onium salt of a polymeric anion.

27 Claims, 1 Drawing Figure

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SUPPORT
CYAN DYE DEVELOPER LAYER
RED-SENSITIVE SILVER HALIDE EMULSION LAYER
INTERLAYER
MAGENTA DYE DEVELOPER LAYER
GREEN-SENSITIVE SILVER HALIDE EMULSION LAYER
INTERLAYER
YELLOW DYE DEVELOPER LAYER
BLUE-SENSITIVE SILVER HALIDE EMULSION LAYER
OVERCOAT LAYER
AQUEOUS ALKALINE PROCESSING COMPOSITION
IMAGE-RECEIVING LAYER
SPACER LAYER
NEUTRALIZING LAYER
SUPPORT

PHOTOGRAPHIC PRODUCTS AND PROCESSES

BACKGROUND OF THE INVENTION

As disclosed in U.S. Pat. No. 2,983,606, issued May 9, 1961, a photosensitive element containing a dye developer, that is, a dye which is a silver halide developing agent, and a silver halide emulsion may be exposed and wetted by a liquid processing composition, for example, by immersion, coating, spraying, flowing, etc., in the dark, and the exposed photosensitive element is superposed prior to, during, or after wetting, on a sheetlike support element which may be utilized as an image-receiving element. In a preferred embodiment, the liquid processing composition is applied to the photosensitive element in a substantially uniform layer as the photosensitive element is brought into superposed relationship with the image-receiving layer. The liquid processing composition, positioned intermediate the photosensitive element and the image-receiving layer, 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 alkaline solutions. It may also be due in part to a tanning effect on the emulsion by oxidized developing agent, and in part to a localized exhaustion of alkali as a result of 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. The image-receiving element receives a depthwise diffusion, from the developer emulsion, of unoxidized dye developer without appreciably disturbing the imagewise distribution thereof to provide the reversed or positive color image of the developed image. The image-receiving element may contain agents adapted to mordant or otherwise fix the diffused, unoxidized dye developer. If the color of the transferred dye developer is affected 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 the desired color. The desired positive image is revealed by stripping the image-receiving layer from the photosensitive element at the end of a suitable imbibition period.

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. A preferred silver halide development function is 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.

Multicolor images may be obtained using color image-forming components such as, for example, the previously mentioned dye developers, in diffusion transfer processes by several techniques. One such technique contemplates obtaining multicolor transfer images utilizing dye developers by employment of an integral multilayer photosensitive element, such as is disclosed in the aforementioned U.S. Pat. No. 2,983,606, and particularly with reference to FIG. 9 of the patent's drawing, wherein at least two selectively sensitized photosensitive strata, superposed on a single support, 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, for example, 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. Each set of silver halide emulsion and associated dye developer strata are disclosed to be optionally separated from other sets by suitable interlayers, for example, by a layer of gelatin or polyvinyl alcohol. In certain instances, it may be desirable to incorporate a yellow filter in front of the green-sensitive emulsion and such yellow filter may be incorporated in an interlayer. However, where desirable, a yellow dye developer of the appropriate spectral characteristics and present in a state capable of functioning as a yellow filter may be employed. In such instances, a separate yellow filter may be omitted.

As disclosed in U.S. Pat. No. 3,362,819, image-receiving elements, particularly adapted for employment in diffusion transfer processes of the type disclosed in aforementioned U.S. Pat. No. 2,983,606, wherein the image-receiving elements are separated from contact with a superposed photosensitive element, subsequent to substantial transfer image formation, preferably comprise a support layer possessing on one surface thereof, in sequence, a polymeric layer which is acidic in character and an image-receiving layer adapted to provide a visible image upon transfer to said layer of diffusible dye image-forming substance, and most preferably include an inert timing or spacer layer intermediate the acidic polymeric layer and the image-receiving layer.

As set forth in the last-mentioned U.S. patent, the acid polymeric layer may comprise polymers which contain acid groups, such as carboxylic acid and sulfonic acid groups, which are capable of forming salts with alkali metals, such as sodium potassium etc., or with organic bases, particularly quaternary ammonium bases, such as tetramethyl ammonium hydroxide, or potentially acid-yielding groups, such as anhydrides or lactones, or other groups which are capable of reacting with bases to capture and retain them. In the preferred embodiments disclosed, the acid polymer contains free carboxyl groups and the transfer processing composition employed contains a large concentration of sodium and/or potassium ions. The acid polymers stated to be most useful are characterized by containing free carboxyl groups, being insoluble in water in the free acid form, and by forming water-soluble sodium and/or potassium salts. One may also employ polymers containing carboxylic acid anhydride groups, at least some of which preferably have been converted to free carboxyl groups prior to imbibition. While the most readily available polymeric acids are derivatives of cellulose or of vinyl polymers, polymeric acids from other classes of polymers may be used. As examples of specific polymeric acids set forth in the application, mention may be made of dibasic acid half-ester derivatives of cellulose which derivatives contain free carboxyl groups, e.g., cellulose acetate hydrogen phthalate, cellulose acetate hydrogen glutarate, cellulose acetate hydrogen succinate, ethyl cellulose hydrogen succinate, ethyl cellulose acetate hydrogen succinate, cellulose acetate hydrogen succinate hydrogen phthalate; ether and ester derivates of cellulose modified with sulfoanhydrides, e.g., with ortho-sulfobenzoic anhydride, polystyrene sulfonic acid; carboxymethyl cellulose; polyvinyl hydrogen phthalate; polyvinyl acetate hydrogen phthalate; polyacrylic acid; acetals of polyvinyl alcohol with carboxy or sulfo substituted aldehydes, e.g., o-, m-, or p-benzaldehyde sulfonic acid or carboxylic acid; partial esters of ethylene/maleic anhydride copolymers; partial esters of methyl-vinyl ether/maleic anhydride copolymers; etc.

The acidic polymer layer is disclosed to contain at least sufficient acid groups to effect a reduction in the pH of the image layer from a pH of about 13 to 14 to a pH of at least 11 or lower at the end of the imbibition period, and preferably to a pH of about 5 to 8 within a short time after imbibition. As previously noted, the pH of the processing composition preferably is of the order of at least 13 to 14.

It is, of course, necessary that the action of the polymeric layer be so controlled as not to interfere with either development of the negative or image transfer of unoxidized dye developers. For this reason, the pH of the image layer is kept at a level of pH 12 to 14 until the dye image has been formed after which the pH is reduced very rapidly to at least about pH 11, and preferably about 9 to 10. Unoxidized dye developers containing hydroquinonyl developing radicals diffuse from the negative to the positive as the sodium or other alkali salt. The diffusion rate of such dye image-forming components thus is at least partly a function of the alkali concentration, and it is necessary that the pH of the image layer remain on the order of 12 to 14 until transfer of the necessary quantity of dye has been accomplished. The subsequent pH reduction, in addition to its desirable effect upon image light stability, serves a highly valuable photographic function by substantially terminating further dye transfer. The processing technique thus effectively minimizes changes in color balance as a result of longer imbibition times in multicolor transfer processes using multilayer negatives.

In order to prevent premature pH reduction during transfer processing, as evidenced, for example, by an undesired reduction in positive image density, the acid component is disclosed to be so distributed in the acidic polymer layer that the rate of its availability to the alkali is controllable, e.g., as a function of the rate of swelling of the polymer layer which rate in turn has a direct relationship to the diffusion rate of the alkali ions. The desired distribution of the acid material in the acid polymer layer may be effected, for example, by mixing an acid polymer with a polymer free of acid groups, or lower in concentration of acid groups, and compatible therewith, or by using only the acid polymer but selecting one having a relatively lower proportion of acid groups. These embodiments are illustrated, respectively, in the cited copending application, by (a) a mixture of cellulose acetate and cellulose acetate hydrogen phthalate and (b) a cellulose acetate hydrogen phthalate polymer having a much lower percentage of phthalyl groups than the first-mentioned cellulose acetate hydrogen phthalate.

It is also disclosed that the layer containing the acid component may contain a water-soluble polymer, preferably a cellulose ester, which acts to control or modulate the rate at which the alkali salt of the acid is formed. As examples of cellulose esters contemplated for use, mention is made of cellulose acetate, cellulose acetate butyrate, etc. The particular polymers and combinations of polymers employed in any given embodiment are, of course, selected so as to have adequate wet and dry strength and when necessary or desirable, suitable subcoats may be employed to help the various polymeric layers adhere to each other during storage and use.

In U.S. Pat. No. 3,362,821, it is also disclosed that the acid polymeric layer may be disposed within the photosensitive element of the film unit intermediate that element's support and next adjacent photosensitive silver halide emulsion layer and associated dye image-providing material, with the optional presence of a spacer or timing layer intermediate the acid layer and next adjacent silver halide emulsion layer.

The inert spacer layer of the last-mentioned U.S. Patents, for example, an inert spacer layer comprising polyvinyl alcohol or gelatin, acts to "time" control the pH reduction by the polymeric acid layer. This timing is disclosed to be a function of the rate at which the alkali diffuses through the inert spacer layer. It was stated to have been found that the pH does not drop until the alkali has passed through the spaced layer, i.e., the pH is not reduced to any significant extent by the mere diffusion into the interlayer, but the pH drops quite rapidly once the alkali diffuses through the spacer layer.

As disclosed in aforementioned U.S. Pat. No. 3,362,819, the presence of an inert spacer layer was found to be effective in evening out the various reaction rates over a wide range of temperatures, for example, by preventing premature pH reduction when imbibition is effective at temperatures above room temperature, for example, at 95° to 100° F. By providing an inert spacer layer, that application discloses that the rate at which alkali is available for capture in the polymeric acid layer becomes a function of the alkali diffusion rates.

However, as disclosed in U.S. Pat. No. 3,445,686, preferably the aforementioned rate at which the cations of the alkaline processing composition, i.e., alkali ions, are available for capture in the polymeric acid layer should be decreased with increasing transfer processing temperatures in order to provide diffusion transfer color processes relatively independent of positive transfer image variations over an extended range of ambient temperatures.

Specifically, it is there stated to have been found that the diffusion rate of alkali through a permeable inert polymeric spacer layer increases with increased processing temperature to the extent, for example, that at relatively high transfer processing temperatures, that is, transfer processing temperatures above approximately 80° F., a premature decrease in the pH of the transfer processing composition occurs due, at least in part, to the rapid diffusion of alkali from the dye transfer environment and its subsequent neutralization upon contact with the polymeric acid layer. This was stated to be especially true of alkali traversing an inert spacer layer possessing permeability to alkali optimized to be effective within the temperature range of optimum transfer processing. Conversely, at temperatures below the optimum transfer processing range, for example, temperatures below approximately 40° F., the last mentioned inert spacer layer was disclosed to provide an effective traverse of the inert spacer layer by alkali having temperature depressed diffusion rates and to result in maintenance of the transfer processing environment's high pH for such an extended time interval as to facilitate formation of transfer image stain and its resultant degradation of the positive transfer images' color definition.

It is further stated in last-mentioned U.S. Pat. No. 3,445,686 to have been found, however, that if the inert spacer layer of the print-receiving element is replaced by a spacer layer which comprises a permeable polymeric layer exhibiting permeability inversely dependent on temperature, that is, a polymeric film-forming material which exhibits decreasing permeability to solubilized alkali derived cations such as alkali metal and quaternary ammonium ions under conditions of increasing temperature, that the positive transfer image defects resultant from the aforementioned overextended pH maintenance and/or premature pH reduction are obviated.

As examples of polymers which were disclosed to exhibit inverse temperature-dependent permeability to alkali, mention may be made of: hydroxypropyl polyvinyl alcohol, polyvinyl methyl ether, polyethylene oxide, polyvinyl oxazolidinone, hydroxypropyl methyl cellulose, isopropyl cellulose, partial acetals of polyvinyl alcohol such as partial polyvinyl butyral, partial polyvinyl formal, partial polyvinyl acetal, partial polyvinyl propional, and the like.

The last-mentioned specified acetals of polyvinyl were stated to generally comprise saturated aliphatic hydrocarbon chains of a molecular weight of at least 1,000, preferably of about 1,000 to 50,000, possessing a degree of acetalation within about 10 to 30 percent, 10 to 30 percent, 20 to 80 percent, and 10 to 40 percent, of the polyvinyl alcohol's theoretical polymeric hydroxyl groups, respectively, and including mixed acetals where desired.

Where desired, a mixture of the polymers is to be employed, for example, a mixture of hydroxypropyl methyl cellulose and partial polyvinyl butyral.

As examples of materials, for use as the image-receiving layer, mention may be made of solution dyeable polymers such as nylon as, for example, N-methoxymethyl polyhexamethylene adipamide; partially hydrolyzed polyvinyl acetate; polyvinyl alcohol with or without plasticizers; cellulose acetate with filler as, for example, one-half cellulose acetate and one-half oleic acid; gelatin; and other materials of a similar nature. Preferred materials comprise polyvinyl alcohol or gelatin containing a dye mordant such as poly-4-vinylpyridine, as disclosed in U.S. Pat. No. 3,148,061, issued Sept. 8, 1964.

As disclosed in the previously cited patents, the liquid processing composition referred to for effecting multicolor diffusion transfer processes comprises at least an aqueous solution of an alkaline material, for example, diethylamine, sodium hydroxide or sodium carbonate and the like, and preferably includes a viscosity-increasing compound constituting a film-forming material of the type which, when the composition is spread and dried, forms a relatively firm and relatively stable film. The preferred film-forming materials disclosed comprise high molecular weight polymers such as polymeric, water-soluble ethers which are inert to an alkaline solution such as, for example, a hydroxyethyl cellulose or sodium carboxymethyl cellulose. Additionally, film-forming materials or thickening agents whose ability to increase viscosity is substantially unaffected if left in solution for a long period of time are also disclosed to be capable of utilization. As stated, the film-forming material is preferably contained in the processing composition in such suitable quantities as to impart to the composition a viscosity in excess of 100 cps. at a temperature of approximately 24° C. and preferably in the order of 100,000 cps. to 200,000 cps. at that temperature.

In accordance with aforementioned U.S. Pat. No. 2,983,606, an image-receiving layer of the type disclosed in that patent need not be separated from its superposed contact with the photosensitive element, subsequent to transfer image formation, if the image-receiving element is transparent and a processing composition containing a substance rendering the dried processing composition layer opaque is spread between the image-receiving layer and the silver halide emulsion or emulsions.

U.S. Pat. No. 3,415,644 also discloses a composite photosensitive structure, particularly adapted for reflection type photographic diffusion transfer color process employment, which comprises a plurality of essential layers including, in sequence, a dimensionally stable opaque layer; one or more silver halide emulsion layers having associated therewith dye image-providing material for providing an imagewise distribution of a dye which is soluble and diffusible, in alkali, at a first pH, as a function of the point-to-point degree of its associated silver halide emulsion's exposure to incident actinic radiation; a polymeric layer adapted to receive solubilized dye image-providing material diffusing thereto; a polymeric layer containing sufficient acidifying capacity to effect reduction of a processing composition from the first pH to a second pH at which the dye image-providing material is substantially nondiffusible; and a dimensionally stable transparent layer, may be exposed to incident actinic radiation and processed by interposing, intermediate the silver halide emulsion layer and the reception layer, an alkaline processing composition possessing the first pH and containing opacifying agent, which may reflect incident radiation, in a quantity sufficient to mask dye image-providing material associated with the silver halide emulsion.

The transfer dye image is viewed, as a reflection image, through the dimensionally stable transparent layer against the background provided by the opacifying agent, distributed as a component of the processing composition, intermediate the reception layer and next adjacent silver halide emulsion layer. The thus-formed opacifying stratum effectively masks residual dye image-providing material retained in association with the silver halide emulsion layer subsequent to processing. Additional film units of this general type are also set forth in U.S. Pat. Nos. 3,573,043; 3,576,625; 3,615,421; and 3,586,501.

U.S. Pat. No. 3,173,786 disclosed and claims color diffusion transfer processes wherein increased density is achieved in the positive image and is primarily the result of increased transfer of the dye developer from unexposed areas of the negative. This increased density is achieved by carrying out the development process in the presence of an onium compound and is believed to be due at least in part to the ability of the onium compounds to increase the solubility of the dye developers, thus effecting control, especially in exposed areas, of the diffusibility of the dye developers.

However, because of the interaction of onium compounds with other reagents in the film unit, the disposition of the onium compounds in the film unit is limited to some degree. For example, care must be taken in disposing the onium compound in the film unit prior to exposure to prevent the onium compound from desensitizing the emulsion.

A novel product has now been found which is not susceptible to the deficiencies of the prior art.

SUMMARY OF THE INVENTION

The present invention is directed to improved photographic products and processes, particularly color diffusion transfer processes, wherein the development of the exposed film unit is carried out in the presence of an onium salt of a polymeric anion. The polymeric nature of the compound permits it to be disposed at various locations in the film unit in a form that renders the onium compound unavailable with respect to interaction with other elements of the film unit. The cation, however, becomes readily available by cation exchange upon contact of the film unit with the alkali of the processing composition when said processing composition is applied to the film unit subsequent to exposure.

BRIEF DESCRIPTION OF THE DRAWING

The FIGURE is a cross-sectional view of the film unit of the present invention.

DETAILED DESCRIPTION OF THE INVENTION

The present invention is directed to products suitable for use in photographic processes, particularly color diffusion transfer processes. The film unit of the present invention, in its preferred embodiment, comprises at least a first silver halide emulsion layer having associated therewith color image-providing materials and an onium salt of a polymeric anion.

As stated above, the employment of onium compounds in color processes, particularly color diffusion transfer processes, is particularly desirable. However, care must be taken in disposing such onium compounds in the film unit to avoid any deleterious reactions. By means of the present invention, it has now been found that an onium salt of a polymeric anion can be disposed in the film unit, either in a separate layer on in another layer in the film unit, which will provide the onium compound at the desired time, that is, during the development of the exposed photosensitive element, but which will be maintained in a photographically inactive or nonreactive state until the processing composition is applied to the film unit, thus insuring the desired degree of stability and sensitivity of the film unit.

Since it is believed that the principle function of the onium compound occurs in the photosensitive element, it is preferred that the onium salt of the polymeric anion be disposed in the photosensitive element and preferably is employed as an overcoat over the photosensitive element or is disposed in the silver halide emulsion.

By means of the present invention, the advantages of processing a photographic silver halide emulsion film unit in the presence of an onium compound to achieve the well-known properties of emulsion speed, accelerated development and enhanced color isolation by virtue of the insolubilizing of oxidized dye developer without the necessity of adding the onium compound with the processing composition. In the prior art when the onium compound is applied to the film unit as a component of the processing composition, efficient use is not made of the entire quantity of onium compound provided. Thus, a portion of the onium compound will remain on the surface of the film unit; in the case of diffusion transfer processing, a portion will migrate into the receiving element or positive layer and a portion must penetrate various layers of the negative to contact the silver halide emulsion and the dye developers in order to carry out its function.

By means of the present invention, the onium compound is disposed in the film unit in or close to the location in which it is to function. As stated above, since it is unavailable or photographically inactive, it can be, if desired, incorporated directly into the silver halide emulsion layer without the well-known detrimental effects normally associated with onium compounds, namely desensitizing at high relative humidity or fogging at low relative humidity. In addition, because it is disposed at or near the specific location that it is to function during processing, loss of onium compound to other portions of the film unit is minimal and its reaction with the appropriate components in the film unit is initiated significantly earlier in the processing. Removing the onium compound from the processing composition also enhances the stability and efficacy of the processing composition by eliminating the possibility of extraneous reactions and instability resulting from the presence of the onium compound.

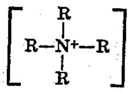
The anion selected for employment in the present invention may comprise substantially any polymeric organic acid, that is, a polymeric backbone having pendant acid groups thereon such as carboxyl groups, sulfonic acid groups, carbonic acid groups and the like. Preferably, the polymeric material selected as the anion will have a relatively low charge density. It should also be understood, however, that the onium salt of a polymeric anion may be diluted with an innocuous diluent such as gelatin.

As examples of suitable materials which may be employed as the polymeric anions, mention may be made of polyvinyl hydrogen phthalate, polyvinyl acrylic acid and carboxymethyl cellulose.

The onium compounds known to the art are employed as the cation in the present invention.

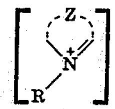
Especially useful results have been obtained through the use of quaternary ammonium compounds. As is known, quaternary ammonium compounds are organic compounds containing a pentavalent nitrogen atom. Generally, they can be considered as derivatives of ammonium compounds wherein the four valences usually 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)



$$\left[R-\overset{\overset{R}{|}}{\underset{\underset{R}{|}}{N^{+}}}-R\right]$$

(2)



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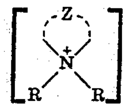


wherein each R is an organic radical and Z represents the atoms necessary to complete a heterocyclic ring. The anion is not shown. As examples of cations within Formulae 1, 2 and 3, mention may be made of tetraethylammonium, N-ethylpyridinium, N,N-diethyl-piperidinium and α-picolinium.

The tertiary sulfonium and quaternary phosphonium compounds may be represented by the formulae:

$$(R)_3S + X^-$$

and

$$(R)_4P + X^-$$

wherein each R is an organic radical, e.g., alkyl, aralkyl, aryl, etc. groups, and X is an anion, e.g., hydroxy, bromide, chloride, toluene sulfonate, etc. As examples of tertiary sulfonium and quaternary phosphonium compounds, mention may be made of lauryldimethylsulfonium p-toluene sulfonate, nonyl-dimethylsulfonium p-toluene sulfonate and octyldimethylsulfonium p-toluene sulfonate, butyldimethyl-sulfonium bromide, triethylsulfonium bromide, tetraethylphosphonium bromide.

Specific cations are set forth in the literature, for example, in U.S. Pat. No. 3,173,786.

The following non-limiting examples illustrate the preparation of the novel onium salts of polymeric anion within the scope of the present invention.

EXAMPLE I

Preparation of N-phenethyl-α-picolinium polyvinylhydrogen phthalate

100 g. (**0.43** mole polymer units) of potassium polyvinyl hydrogen phthalate in 2 liters of water was mixed with 250 g. of N-phenethyl-α-picolinium bromide (**0.76** mole) in 500 ml. of water. The resulting solution was dialyzed with distilled water until a negative silver nitrate test was observed. This final mixture was freeze-dried to yield polyvinyl hydrogen phthalate with 25 percent.

$$\left(\frac{\text{mole cation}}{\text{mole cation and mole polymer units}}\right)$$

α-picolinium cation substitution. The IR, NMR and UV spectra of the white polymeric product was consistent with the structure of phenethyl-α-picolinium polyvinyl hydrogen phthalate. Analysis:

Theory: 3.6 percent N
Found: 2.7 percent N

EXAMPLE II

Preparation of benzyl-α-picolinium salt of polyvinyl hydrogen phthalate

The procedure was essentially the same as that set forth in Example I except that benzyl-α-picolinium bromide was used instead of N-phenethyl-α-picolinium brmoide.

Analysis:
Theory: 3.9 percent N
Found: 3.1 percent N

EXAMPLE III

Preparation of N-phenethyl-α-picolinium salt poly(acrylic acid)

The procedure was essentially the same as that described in Example I except that the ammonium salt of poly acrylic acid was used as anion sources instead of potassium polyvinyl hydrogen phthalate.

EXAMPLE IV

Preparation of N-phenethyl-α-picolinium salt of carboxymethyl cellulose

The procedure was essentially the same as that described in Example I except that the sodium salt of carboxymethyl cellulose was used as anion source instead of potassium polyvinyl hydrogen phthalate.

Reference is now made to the drawing wherein there is illustrated a film unit of the present invention.

As illustrated in the drawing, film unit **10** comprises rupturable container **11**, retaining, prior to processing, aqueous alkaline solution **12**, and photosensitive laminate **13** including, in order, dimensionally stable support layer **14**, preferably a flexible sheet material; cyan dye developer layer **15**; red-sensitive halide emulsion layer **16**; interlayer **17**; magenta dye developer layer **18**; green-sensitive silver halide emulsion layer **19**; interlayer **20**; yellow dye developer layer **21**; blue-sensitive silver halide emulsion layer **22**; auxiliary layer **23**, which may contain an auxiliary silver halide developing agent; and an image-receiving element **28** including image-receiving layer **24**; spacer layer **25**; neutralizing layer **26**; and dimensionally stable support layer **27**, preferably a flexible sheet material.

Rupturable container **11** may be of the type shown and described in any of U.S. Pat. Nos. 2,543,181; 2,634,886; 2,653,732; 2,723,051; 3,056,492; 3,056,491; 3,152,515; and the like. In general, such containers will comprise a rectangular blank of fluid- and air-impervious material folded longitudinally upon itself to form two walls **29** which are sealed to one another along their longitudinal and end margins to form a cavity in which processing solution **12** is retained. The longitudinal marginal seal **30** is made weaker than the end seals so as to become unsealed in response to the hydraulic pressure generated within the fluid contents **12** of the container by the application of compressive pressure to walls **29** of the container.

As illustrated in the drawing, container **11** is fixedly positioned and extends transverse a leading edge of laminae **13** and **28** whereby to effect unidirectional discharge of the container's contents **12** between image-receiving layer **24** and the stated layer next adjacent thereto, upon application of compressive force to container **11**. Thus, container **11**, as illustrated, is positioned and extends transverse a leading edge of laminae **13** and **28** with its longitudinal marginal seal **30** directed toward the interface between image-receiving layer **28** and auxiliary layer **23**. As previously mentioned, the fluid contents of the container comprise an aqueous alkaline solution having a pH at which the dye developers are soluble and diffusible.

In the performance of a diffusion transfer multicolor process employing film unit **10**, the unit is exposed to radiation, actinic to photosensitive laminate **13**.

Subsequent to exposure, film unit **10** is processed by being passed through opposed suitably gapped rolls **35** in order to apply compressive pressure to frangible container **11** and to effect rupture of longitudinal seal **30** and distribution of alkaline processing composition **12**, having a pH at which the cyan, magenta and yellow dye developers are soluble and diffusible, intermediate dyeable polymeric layer **24** and auxiliary layer **23**.

Alkaline processing solution **12** permeates emulsion layers **16**, **19** and **22** to initiate development in the respective emulsions, the cyan magenta and yellow dye developers of layers **15**, **18** and **21** are immobilized, as a function of the development of their respective associated silver halide emulsions, preferably substantially as a result of their conversion from the reduced form to their relatively insoluble and nondiffusible oxidized form, there providing imagewise distributions of mobile, soluble and diffusible cyan, magenta and yellow dye developer, as a function of the point-to-point degree of their associated emulsions' exposure. At least part of the imagewise distributions of mobile cyan, magenta and yellow dye developer transfers, by diffusion, to aqueous alkaline solution permeable polymeric layer **24** to provide a multicolor dye transfer image to that layer. Subsequent to substantial transfer image formation, a sufficient portion of the ions comprising aqueous alkaline solution **12** transfers, by diffusion, through permeable polymeric layer **24**, permeable spacer layer **25** and to permeable polymeric acid layer **26** whereby alkaline solution **12** decreases in pH, as a function of neutralization, to a pH at which the cyan, magenta and yellow dye developers, in the reduced form, are insoluble and nondiffusible, to provide thereby a stable multicolor dye transfer image.

Subsequent to substantial transfer image formation, print-receiving element **28** may be manually dissoci-

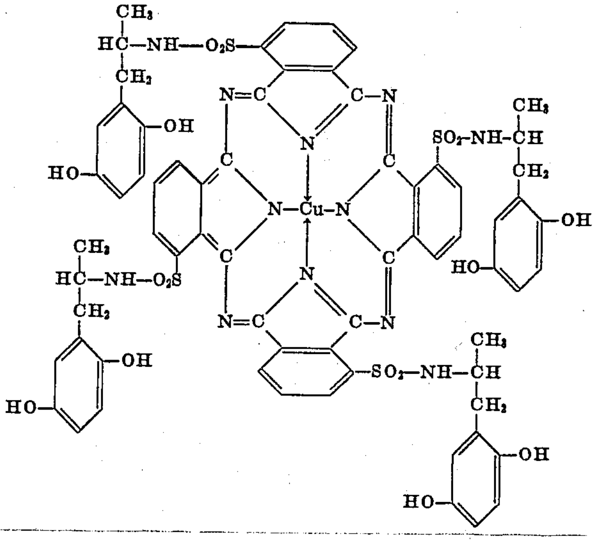
by stripping or if film units of the described U.S. Pat. Nos. 3,594,194 and 3,594,165 are employed, the film unit is a permanent laminate.

As stated above, the onium compound may be employed in a variety of locations in the film unit. For example, it may be disposed in one or more of the emulsion or dye layers or it may comprise overcoat layer **23**. It is preferred that the onium compound be disposed in the emulsion layer.

The present invention will be further illustrated and detailed in conjunction with the following illustrative construction which sets out a representative embodiment and photographic utilization of the novel photographic film units of this invention, which, however, are not limited to the details therein set forth and are intended to be illustrative only.

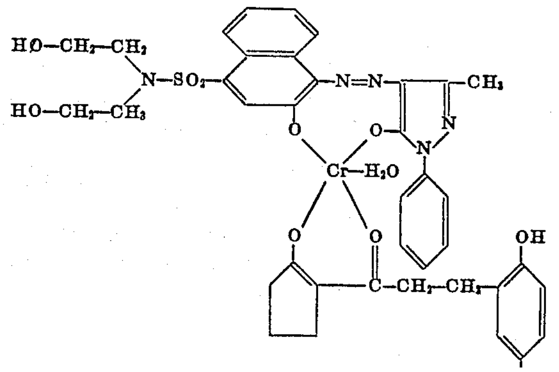
A film unit within the scope of the present invention may be prepared, for example, by coating, in succession, on a gelatin subbed, 4 mil. opaque polyethylene terephthalate film base, the following layers:

1. a layer of the cyan dye developer



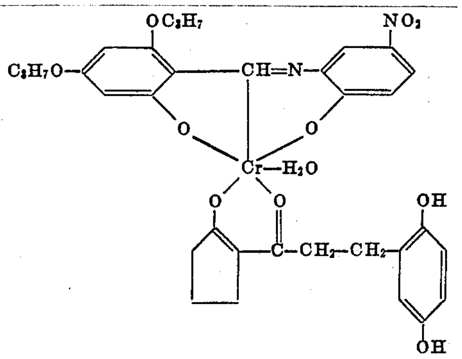
dispersed in gelatin and coated at a coverage of about 98 mgs./ft.^{2} of dye and about 92 mgs./ft.^{2} of gelatin;

2. a red-sensitive gelatino-silver iodochlorobromide emulsion coated at a coverage of about 225 mgs./ft.^{2} of silver and about 50 mgs./ft.^{2} of gelatin;
3. a layer of butyl acrylate/diacetone acrylamide/styrene/methacrylic acid (60/30/4/6) coated at a coverage of about 136 mgs./ft.^{2} and polyacrylamide at a coverage of about 4.3 mgs./ft.^{2};
4. a layer of the magenta dye developer



dispersed in gelatin and coated at a coverage of about 71 mgs./ft.^{2} of dye and about 50 mgs./ft.^{2} of gelatin;

5. a green-sensitive gelatino-silver iodochlorobromide emulsion coated at a coverage of about 80 mgs./ft.^{2} of silver and 40 mgs./ft.^{2} of gelatin;
6. a layer comprising butyl acrylate/—diacetone acrylamide/styrene/methacrylic acid (60/30/—4/6) coated at a coverage of about 95 mgs./ft.^{2} and polyacrylamide coated at a coverage of about 12 mgs./ft.^{2};
7. a layer of the yellow dye developer



and the auxiliary developer 4'-methylphenyl hydroquinone dispersed in gelatin and coated at a coverage of about 81 mgs./ft.^{2} of dye, about 15 mgs./ft.^{2} of auxiliary developer and 54 mgs./ft.^{2} of gelatin;

8. a blue-sensitive gelatino-silver iodochlorobromide emulsion coated at a coverage of about 65 mgs./ft.^{2} of silver and about 33 mgs./ft.^{2} of gelatin having therein 4'-methylphenyl hydroquinone coated at a coverage of about 30 mgs./ft.^{2}; and
9. a layer of phenethyl-α-picolinium polyvinyl hydrogen phthalate coated at a coverage of about 200 mgs./ft.^{2}.

Then a transparent 5 mil. polyester film base may be coated, in succession with the following illustrative layers:

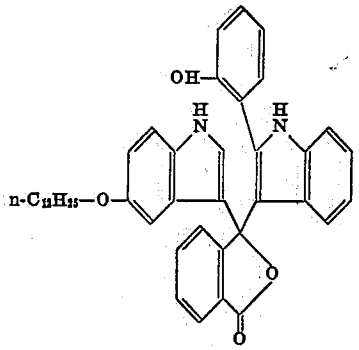
1. a 7:3 mixture, by weight, of polyethylene/—maleic acid copolymer and polyvinyl alcohol at a coverage of about 1,400 mgs./ft.^{2}, to provide a polymeric acid layer;
2. a graft copolymer of acrylamide and diacetone acrylamide on a polyvinyl alcohol backbone in a molar ratio of 1:3.2:1 at a coverage of about 300 mgs./ft.^{2}, to provide a polymeric spacer layer; and
3. a 2:1 mixture, by weight, of polyvinyl alcohol and poly-4-vinylpyridine, at a coverage of about 900 mgs./ft.^{2} and including about 20 mgs./ft.^{2} phenylmercapto-tetrazole, to provide a polymeric image-receiving layer.

The two components thus prepared may then be taped together in laminate form, at their respective edges, by means of a pressure-sensitive binding tape extending around, in contact with, and over the edges of the resultant laminate.

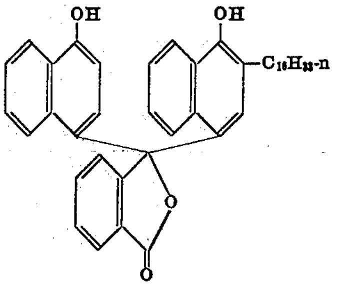
A rupturable container comprising an outer layer of lead foil and an inner liner or layer of polyvinyl chloride retaining an aqueous alkaline processing solution comprising:

Water	100	cc.
Potassium hydroxide	11.2	gms.
Hydroxyethyl cellulose (high viscosity) [commercially available from Hercules Powder Co., Wilmington, Delaware, under the trade name Natrasol 250]	3.4	gms.
Benzotriazole	1.15	gms.
Titanium dioxide	50.0	gms.

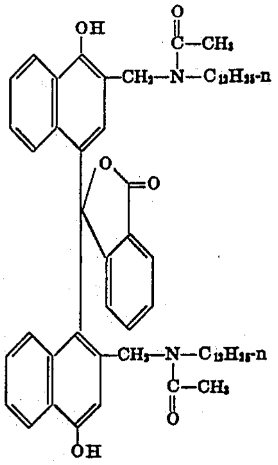
(A) 2.08 gms.



(B) 0.52 gms.



(C) 1.18 gms.



may then be fixedly mounted on the leading edge of each of the laminates, by pressure-sensitive tapes interconnecting the respective containers and laminates, such that, upon application of compressive pressure to a container, its contents may be distributed, upon rupture of the container's marginal seal, between the polymeric image-receiving layer and next adjacent gelatin layer.

The photosensitive composite film units may be exposed through step wedges to selectively filter radiation incident on the transparent polyethylene terephthalate layer and processed by passage of the exposed film units through appropriate pressure-applying members, such as suitably gapped, opposed rolls, to effect rupture of the container and distribution of its contents. During processing, the multicolor dye transfer image formation may be viewed through the transparent polyethylene terephthalate layer against the titanium dioxide background provided by distribution of the pigment containing processing composition between Layer **9** and the polymeric image-receiving layer.

The results obtained with the above-described film unit were compared with a film unit of similar construction wherein Layer **9** comprised the potassium salt of polyvinyl hydrogen phthalate at a coverage of about 145 mgs./ft.^{2} and N-phenethyl-α-picolinium bromide in the processing composition at a level of 0.34 mmoles/ft.^{2}. Comparable photographic results in terms of color isolation and increased density in the positive image were achieved between the film unit of the present invention and the above-described film unit where the quaternary ammonium salt was disposed in the processing composition. In addition, less quaternary ammonium compound was employed in the present invention to achieve the same results since more efficient use could be made thereof. In a film unit employing the N-phenethyl-α-picolinium bromide in Layer **9**, however, total fogging of the negative was observed.

More specifically, in comparing the above-described film unit of the present invention with the above-described control film unit, it was noted in an analysis of the yellow column that although there was slightly less blue absorption in the D_{max}, there was less yellow dye drop-off particularly in the mid regions of the yellow column. Higher red shoulder speed was also noted. In the magenta column, a slight green absorption loss was noted in the D_{max}, but improved magenta saturation elsewhere. A lower red D_{max} and increased shoulder speed resulted in superior cyan clean-out in the shoulder regions. In the cyan column, improved cyan saturation was noted. A slight blue and green speed decrease was also observed. Improved magenta saturation was observed in the blue column. In the green column, there was an improved ratio of cyan to yellow with very little cyan and yellow drop-off. However, a slight increase over the control of magenta contamination was noted. In the red column, improved magenta saturation and richer reds were noted, as well as higher red shoulder speed and better cyan clean-out in mid and shoulder regions. In the neutral column, good reproduction of blacks although slightly warm reproduction of grays and whites was noted. The slopes of the red, green and blue curves are significantly better matched than were those of the control film unit.

It will be noted that the liquid processing composition employed may contain an auxiliary or accelerating developing agent, such as p-methylaminophenol, 2,4-diamino-phenol, p-benzylaminophenyl, hydroquinone, toluhydroquinone, phenylhydroquinone, 4′-methylphenylhydroquinone, etc. 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 in U.S. Pat. No. 3,039,869, issued June 19, 1962. As examples of suitable combinations 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 any one or more of the silver halide emulsion strata, the strata containing the dye developers, the interlayers, the overcoat layer, the image-receiving layer, or in any other auxiliary layer, or layers, of the film unit. 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 product of an oxidized auxiliary developing agent, the latter developing agent being oxidized by the development of exposure 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.

It will be apparent that the relative proportions of the agents of the diffusion transfer processing composition may be altered to suit the requirements of the operator. Thus, it is within the scope of this invention to modify the herein described developing compositions by the substitution of preservatives, alkalies, etc., other than those specifically mentioned, provided that the pH of the composition is initially at the first pH and solvent concentration required. When desirable, it is also contemplated to include, in the developing composition, components such as restrainers, accelerators, etc. Similarly, the concentration of various components may be varied over a wide range and when desirable adaptable components may be disposed in the photosensitive element, prior to exposure, in a separate permeable layer of the photosensitive element and/or in the photosensitive emulsion.

An extensive compilation of specific dye developers particularly adapted for employment in photographic diffusion transfer processes is set forth in aforementioned U.S. Pat. No. 2,983,606 and in the various copending U.S. applications referred to in that patent, especially in the table of U.S. applications incorporated by reference into the patent as detailed in column **27**. As examples of additional U.S. patents detailing specific dye developers for photographic transfer process use, mention may also be made of U.S. Pat Nos. 2,983,605; 2,992,106; 3,047,386; 3,076,808; 3,076,820; 3,077,402; 3,126,280; 3,131,061; 3,134,762; 3,134,765; 3,135,604; 3,135,605; 3,135,606; 3,135,734; 3,141,772; 3,142,565; and the like.

Although the invention has been discussed in detail throughout employing dye developers, the preferred image-providing materials, it will be readily recognized that other, less preferred, image-providing materials may be substituted in replacement of the preferred dye developers in the practice of the invention. For example, there may be employed dye image-forming materials such as those disclosed in U.S. Pat. Nos. 2,647,049; 2,661,293; 2,698,244; 2,698,798; 2,802,735; 3,148,062; 3,227,550; 3,227,551; 3,227,552; 3,227,554; 3,243,294; 3,330,655; 3,347,671; 3,352,672; 3,364,022; 3,443,939; 3,443,940; 3,443,941; 3,443,943; etc., wherein color diffusion transfer processes are described which employ color coupling techniques comprising, at least in part, reacting one or more color developing agents and one or more color formers or couplers to provide a dye transfer image to a superposed image-receiving layer and those disclosed in U.S. Pat. Nos. 2,774,668 and 3,087,817, wherein color diffusion transfer processes are described which employ the imagewise differential transfer of complete dyes by the mechanisms therein described to provide a transfer dye image to a contiguous image-receiving layer, and thus including the employment of image-providing materials in whole or in part initially insoluble or nondiffusible as disposed in the film unit which diffuse during processing as a direct or indirect function of exposure.

For the production of the photosensitive gelatino silver halide emulsions employed to provide the film unit, the silver halide crystals may be prepared by reacting a water-soluble silver salt, such as silver nitrate, with at least one water-soluble halide, such as ammonium, potassium or sodium bromide, preferably together with a corresponding iodide, in an aqueous solution of a peptizing agent such as a colloidal gelatin solution; digesting the dispersion at an elevated temperature, to provide increased crystal growth; washing the resultant water-soluble salts by chilling the dispersion, noodling the set dispersion, and washing the noodles with cold water, or alternatively, employing any of the various flocc systems, or procedures, adapted to effect removal of undesired components, for example, the procedures described in U.S. Pat. Nos. 2,614,928; 2,614,929; 2,728,662; and the like; after-ripening the dispersion at an elevated temperature in combination with the addition of gelatin and various adjuncts, for example, chemical sensitizing agents of U.S. Pat Nos. 1,574,944; 1,623,499; 2,410,689; 2,597,856; 2,597,915; 2,487,850; 2,518,698; 2,521,926; and the like; all according to the traditional procedures of the art, as described in Neblette, C. B., *Photography Its Materials and Processes*, sixth Ed., 1962.

Optical sensitization of the emulsion's silver halide crystals may be accomplished by contact of the emulsion composition with an effective concentration of the selected optical sensitizing dyes dissolved in an appropriate dispersing solvent such as methanol, ethanol, acetone, water, and the like; all according to the traditional procedures of tha art, as described in Hammer, F. M., *The Cyanine Dyes and Related Compounds*.

Additional optional additives, such as coating aids, herdeners, viscosity-increasing agents, stabilizers, preservatives, and the like, for example, those set forth hereinafter, also may be incorporated in the emulsion formulation, according to the conventional procedures known in the photographic emulsion manufacturing art.

The photoresponsive material of the photographic emulsion will, as previously described, preferably comprise a crystal of silver, for example, one or more of the silver halides such as silver chloride, silver iodide, silver bromide, or mixed silver halides such as silver chlorobromide, silver chloroiodobromide or silver iodobromide, of varying halide ratios and varying silver concentrations.

As the binder for the respective emulsion strata, the aforementioned galatin may be, in whole or in part, replaced with some other colloidal material such as albumin; casein; or zein; or resins such as a cellulose derivatives, as described in U.S. Pat. Nos. 2,322,085 and 2,327,808; polyacrylamides, as described in U.S. Pat. No. 2,541,474; vinyl polymers such as described in an extensive multiplicity of readily available U.S. and foreign patents.

Although the preceding description of the invention has been couched in terms of the preferred photosensitive component construction wherein at least two selectively sensitized photosensitive strata are in contiguous coplanar relationship and, specifically, in terms of the preferred tripack type structure comprising a red-sensitive silver halide emulsion stratum, a green-sensitive silver halide emulsion stratum and a blue-sensitive silver halide emulsion stratum having associated therewith, respectively a cyan dye developer, a magenta dye developer and a yellow dye developer, the photosensitive component of the film unit may comprise at least two sets of selectively sensitized minute photosensitive elements arranged in the form of a photosensitive screen wherein each of the minute photosensitive elements has associated therewith, for example, an appropriate dye developer in or behind its respective silver halide emulsion portion. In general, a suitable photosensitive screen will comprise 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, a magenta and a yellow dye developer.

The present invention also includes the employment of a black dye image-providing material and the use of a mixture of dye image-providing material adapted to provide a black-and-white transfer image, for example, the employment of dye developers of the three subtractive colors in an appropriate mixture in which the quantities of the dye developers are proportioned such that the colors combine to provide black.

Where in 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 emulsion layers. 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 emulsion layers will be a positive and the dye 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 addition to the described essential layers, it will be recognized that the film unit may also contain one or more subcoats or layers, which, in turn, may contain one or more additives such as plasticizers, intermediate essential layers for the purpose, for example, of improving adhesion, and that any one or more of the described layers may comprise a composite of two or more strata of the same, or different, components and which may be contiguous, or separated from, each other, for example, two or more neutralizing layers or the like, one of which may be disposed intermediate the cyan dye image-forming component retaining layer and the dimensionally stable opaque layer.

Since certain changes may be made in the above product and 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 drawings shall be interpreted as illustrative and not in a limiting sense.

What is claimed is:

1. A photographic film unit comprising a photosensi-

tive element comprising at least one silver halide emulsion having associated therewith a dye image-providing material and an onium salt of a polymeric anion.

2. A film unit as defined in claim **1** which includes a support carrying on a surface a plurality of photosensitive silver halide emulsions, each of said emulsions having associated therewith a dye which is a silver halide developing agent and at least one of said emulsions having additionally associated therewith an onium salt of a polymeric anion.

3. A product as defined in claim **1** wherein said onium salt of a polymeric anion is disposed in at least one of said silver halide emulsions.

4. A product as defined in claim **1** wherein said onium salt of a polymeric anion is disposed in a separate layer overlying said silver halide emulsions.

5. A product as defined in claim **1** wherein said onium salt is a quaternary ammonium salt.

6. A product as defined in claim **5** wherein said quaternary ammonium salt of a polymeric anion is N-phenethyl-α-picolinium polyvinyl hydrogen phthalate.

7. A product as defined in claim **5** wherein said onium salt of a polymeric anion is N-phenethyl-α-picolinium carboxymethyl cellulose.

8. A product as defined in claim **5** wherein said onium salt of a polymeric anion is benzyl-α-picolinium polyvinyl hydrogen phthalate.

9. A product as defined in claim **5** wherein said onium salt of a polymeric anion is N-phenethyl-α-picolinium polyvinyl acrylic acid.

10. A product as defined in claim **5** wherein said onium salt of a polymeric anion is present at a level of about 50 mg./ft.^{2} to 400 mg./ft.^{2}.

11. A process for forming a transfer image in color which comprises exposing a photosensitive element comprising at least one silver halide emulsion having associated therewith an onium salt of a polymeric anion and a color providing material, developing said exposed photosensitive element, and transferring at least a portion of an imagewise distribution of said color-providing material to a superposed image-receiving layer.

12. A process as defined in claim **11** which comprises exposing a photosensitive element comprising at least one silver halide emulsion, each of said silver halide emulsions having associated therewith a dye which is a silver halide developing agent and at least one of said silver halide emulsions having additionally associated therewith an onium salt of a polymeric anion, developing said exposed photosensitive element, forming in undeveloped areas of each of said silver halide emulsions as a function of development, an imagewise distribution of associated dye developer in unoxidized diffusible condition and transferring by diffusion at least a portion of said imagewise distribution of unoxidized dye developer to a superposed image-receiving layer to form said color transfer image.

13. A process as defined in claim **12** wherein said onium salt of a polymeric anion is disposed in at least one of said silver halide emulsions.

14. A process as defined in claim **12** wherein said onium salt of a polymeric anion comprises a layer overlying said silver halide emulsions.

15. A process as defined in claim **12** wherein said onium salt is a quaternary ammonium salt.

16. A process as defined in claim **12** wherein said photosensitive element 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, each of said silver halide emulsions having associated therewith, respectively, a cyan dye developer, a magenta dye developer and a yellow dye developer, each of said dye developers disposed in an alkali permeable layer behind its associated silver halide emulsion.

17. A photographic product comprising a photosensitive element, said photosensitive element comprising a support carrying at least one silver halide emulsion, each of said silver halide emulsions having associated therewith a dye which is a silver halide developing agent, at least one of said silver halide emulsions additionally having associated therewith an onium salt of a polymeric anion, an image-receiving element comprising a support carrying an image-receiving layer and a rupturable container releasably holding an aqueous alkaline processing solution, said photosensitive element and said image-receiving element being capable of being superposed on each other with said rupturable container positioned therebetween so as to release said processing solution upon rupture of said container to permeate said silver halide emulsions and said image-receiving layer.

18. A composite photographic diffusion transfer color process film unit which comprises, in combination:

a. a photosensitive laminate containing, as essential layers, a dimensionally stable transparent support carrying on one surface, in order, a dyeable polymeric layer, a processing composition permeable opaque layer, and a photosensitive silver halide layer having associated therewith a dye image-forming material which is processing composition diffusible, as a function of the point-to-point degree of silver halide layer's exposure to actinic radiation; and having additionally associated therewith an onium salt of a polymeric anion;

b. a transparent dimensionally stable sheet superposed substantially coextensive the surface of the laminate opposite the dimensionally stable transparent support; and

c. a rupturable container retaining a processing composition including an opacifying agent positioned extending transverse a leading edge of the film unit to effect unidirectional discharge of the container's contents intermediate the dimensionally stable sheet and the photosensitive laminate.

19. A photographic film unit as defined in claim **18** wherein said dyeable polymeric layer is processing composition permeable and said film unit additionally includes a polymeric layer, containing sufficient acidifying capacity to effect reduction of a processing composition having a first pH at which said dye image-forming material is soluble and diffusible to a second pH at which said material is substantially nondiffusible, positioned intermediate said dimensionally stable transparent support and next adjacent essential layer.

20. A photographic film unit as defined in claim **18** wherein said opacifying agent is present in said processing composition in a quantity effective, upon distribution on the surface of said photosensitive laminate, to prevent exposure of said photosensitive silver halide layer during processing in the presence of radiation actinic thereto and incident on distributed processing composition and said opaque layer is effective to prevent exposure of said photosensitive silver halide layer during processing in the presence of radiation actinic thereto and incident on said opaque layer.

21. A product as defined in claim **18** wherein said onium salt of a polymeric anion is disposed in at least one of said silver halide emulsions.

22. A product as defined in claim **18** wherein said onium salt of a polymeric anion comprises a layer intermediate said photosensitive silver halide emulsion layer and said dyeable polymeric layer.

23. A photographic film unit as defined in claim **18** which is adapted to be processed by passing said unit between a pair of juxtaposed pressure-applying members and which includes, in combination:

a photosensitive laminate containing, as essential layers, at least two selectively sensitized silver halide emulsion layers each having a dye, which dye is a silver halide developing agent, of predetermined color associated therewith, at least one of said silver halide emulsion layers additionally having associated therewith an onium salt of a polymeric anion, each of said dyes soluble and diffusible, in alkali, at a first pH, an alkaline solution permeable polymeric layer dyeable by said dyes, an alkaline solution permeable opaque layer positioned intermediate said dyeable polymeric layer and the silver halide emulsion layer next adjacent thereto, a dimensionally stable alkaline solution impermeable transparent layer, and an alkaline solution permeable transparent polymeric acid layer containing sufficient acidifying groups to effect reduction of a processing solution having said first pH to a second pH at which said dyes are nondiffusible positioned intermediate said dimensionally stable transparent layer and the essential layer next adjacent thereto;

a dimensionally stable transparent sheet superposed coextensive the surface of the laminate opposite said dimensionally stable transparent layer; and

a rupturable container retaining an aqueous alkaline processing solution containing an opacifying agent, having said first pH fixedly positioned and extending transverse said leading edge of said laminate to effect unidirectional discharge of the container's contents coextensive the surface of the laminate intermediate said laminate and said transparent sheet.

24. A product as defined in claim **18** wherein each of said silver halide emulsion layers has an onium salt of a polymeric anion disposed therein.

25. A product as defined in claim **18** wherein said photosensitive laminate includes a layer of an onium salt of a polymeric anion position intermediate said dyeable polymeric layer and the silver halide emulsion layer next adjacent thereto.

26. A product as defined in claim **23** wherein said onium salt is a quaternary ammonium salt.

27. A product as defined in claim **26** wherein said quaternary ammonium salt of a polymeric anion is N-phenethyl-α-picolinium polyvinyl hydrogen phthalate.

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