Dec. 19, 1967 F. VIRO **3,359,104**

COLOR DIFFUSION TRANSFER PROCESS AND NEGATIVE MATERIAL THEREOF

Filed Dec. 30, 1963

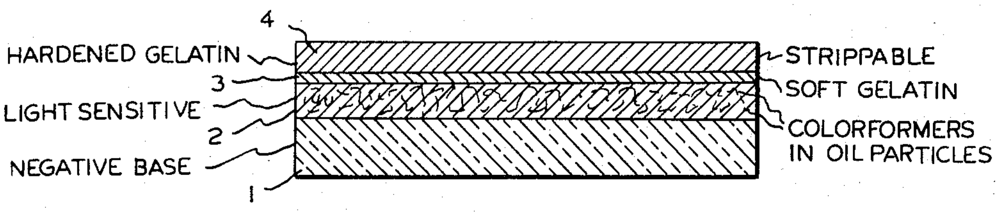

FIG.1

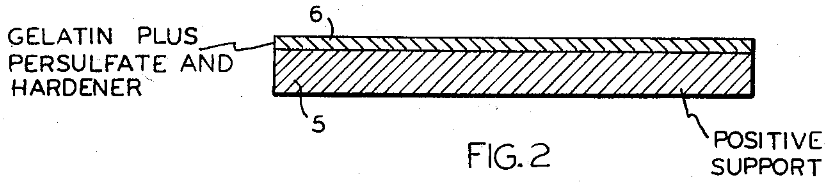

FIG. 2

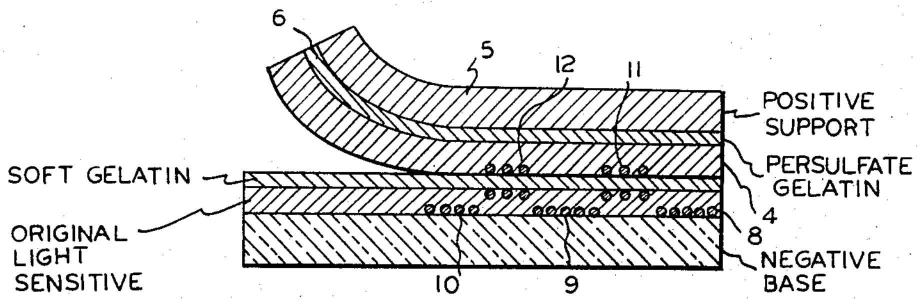

FIG.3

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COLOR DIFFUSION TRANSFER PROCESS AND NEGATIVE MATERIAL THEREOF

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8 Claims. (Cl. 96—29)

The present invention relates to color photography and more particularly to a color diffusion transfer process by which unreacted color former(s) in the unexposed or partially exposed areas of a color negative are diffused image-wise, after color developing the negative, into a hardened, strippable, hydrophilic colloid layer carried on the front emulsion of the color negative and physically transferring said layer to a receiving sheet while causing the diffused color former(s) in said layer to react with oxidized color developer to produce positive dye images.

Systems are known using mono- or multilayer coatings containing differently sensitized silver halide emulsions and corresponding color formers capable of yielding dyes complementary in color to the light rays to which each emulsion is sensitized, the color former(s) being incorporated and dispersed in resinous or oily packets throughout the emulsion with the silver halide grains either incorporated in the colloidal carrier (gelatin or gelatin substitute) of the emulsion, or in the resinous packets, or in both. The technique based on this process is generally referred to as "packet" or "mixed grain emulsion" technique. Such technique is described, for example, in U.S. application Ser. No. 693,998, now abandoned, filed Nov. 1, 1957 by Schwerin et al., in British Patent 718,404, French Patent 1,080,967 and U.S. Patents 2,490,749, 2,544,640, 2,678,794, 2,698,795, 2,698,796, 2,698,797 2,796,544 and 2,322,027. These patents and applications indicate the steps to be followed and the oils to be used in preparing the "packet" or "mixed grain emulsions."

It has been suggested in U.S. application Ser. No. 279,033, now abandoned, filed by A. K. Schwerin et al. on Apr. 25, 1963, that such emulsion coating(s) in which, however, special color formers are employed may constitute a color negative diffusion transfer material by which after exposure and color development of the coatings(s), image-wise diffusion of the unreacted color former(s) directly to a receiving sheet is effected by controlling the pH of the environment around and adjacent to the unreacted color formers. By including an oxidizing agent in the receiving sheet, dyes are formed image-wise in the sheet through reaction of the oxidizing agent, color developer and diffused color former(s).

In commercial photography, the color formers which are employed in the sensitized emulsion layers are either of the hydrophilic type, i.e., solubilized by alkalies at low pH or of the hydrophobic or lipophilic type, i.e., dissolved in oils of the type described in U.S. Patent 2,322,027, and are of such high molecular weight that they resist diffusion from the emulsions even at a high pH. The color former(s) employed in the above diffusion transfer procedure and which have been characterized as of a special type, partake in part of the characteristics of the lipophilic color formers of the prior art, but are of a much lesser molecular weight so that at high pH, i.e., 12.5–13, they are diffusible in an aqueous medium. Specifically, such color formers must possess the following attributes: (1) medium molecular weight, (2) freedom from water solubilizing groups, such as carboxy or sulfonic acid groups, (3) sufficient oil solubility to be incorporated in resinous or oily packets, (4) contain such groups which only at a high pH (12.5–13) are able to form an alkali metal salt which renders the color former molecule diffusible in aqueous medium, i.e., groups such as phenolic hydroxy and enolic hydroxyl, and (5) produce non-diffusible dyes with conventional primary aromatic amino color developing agents, such as N-diethyl-p-phenylenediamine; N-ethyl - N - hydroxyethyl-p-phenylenediamine and N-diethyl-3-methyl-p-phenylenediamine and the like.

This rather unique method of color image transfer unfortunately will not operate in a multilayer color system. In addition, the color reproduced in the receiving sheet leaves much to be desired particularly from the standpoint of color density. Washing of the reproduced image and color stain upon standing must also be dealt with. Finally, control over diffusion of the color formers and oxidation of the developer in the transfer sheet pose additional problems.

It has now been discovered that the disadvantages of said color diffusion process may be avoided and that colored images including multi-colored images can be obtained in a receiving sheet with improved color density and without stain by providing a negative material having a silver halide emulsion containing color formers dispersed in a crystalloidal material as aforesaid, overcoating the emulsion with a hardened, strippable hydrophilic colloid, providing a receiving sheet comprising a base coated with a hydrophilic colloid containing a diffusible oxidizing agent, exposing the negative to an image and color developing the same, forcing the hardened, strippable hydrophilic colloid layer of the negative into contact with the hydrophilic colloid layer of the receiving sheet at a pH 12.5 to 13 to cause image-wise diffusion of the unreacted color formers into the hardened, strippable hydrophilic colloid layer and diffusion of the oxidizing agent into said layer and reacting oxidized developer in said layer with the color formers to produce color images.

By this procedure it is clear that the hardened, strippable hydrophilic colloid becomes the locus of the reaction leading to the formation of the dye images. In other words, oxidation of the developer by the oxidizing agent and reaction of the oxidized developer with the diffused color formers occur solely in said layer. This provides for a control not heretofore possible in the diffusion transfer process involving my image-wise migration of the color formers from the silver halide emulsion layer under an adjustment of pH. By peeling the receiving sheet from the negative, the hardened, strippable colloid layer is physically transferred to the receiving sheet to which it tenaciously adheres. The images formed do not require washing and are stain free.

Such negative color material, transfer sheet, and said said method of producing color images in the transfer sheet constitutes the purposes and objects of my invention.

The invention will be better understood by reference to the accompanying drawing in which

FIGURE 1 is a sectional view of the color negative material.

FIGURE 2 is a transverse section of the receiving sheet and FIGURE 3 shows the superimposition and the stripping step leading to the transfer of the strippable layer from the color negative to the sheet.

The negative color material comprises a base **1** which carries a light-sensitive silver halide emulsion **2** in which are incorporated special color formers dispersed in a crystalloidal material as described in Jelley, U.S.P. 2,322,027. It is to be understood that in lieu of a single silver halide emulsion layer **2**, two or more superimposed emulsion layers may be employed. For example, a three-layer material may contain an innermost emulsion with a special color former for cyan, an intermediate emulsion layer with a special color former for magenta, and outer with a special color former for yellow, each emulsion being sensitized to a primary color. The outermost emulsion layer or layer **2**, as the case may be, is overcoated with a thin, soft hydrophilic colloid layer **3**, shown in the drawing as soft gelatin. Other water soluble colloids such as PVA, PVP, or methyl cellulose may be used in lieu of gelatin. This partition layer **3** is in turn overcoated with a hardened strippable hydrophilic colloid layer **4** of gelatin, PVA, PVP or methyl cellulose. Hardening may be effected by use of a conventional hardener such as formaldehyde, mucochloric acid or the like. This layer due to the partition layer **3** is readily strippable from the negative, when moistened, simple by pressing it in contact with a dry adhesive layer.

The negative color material is designed to cooperate with the receiving sheet of FIGURE 2 in which **5** is the base and **6** is a hydrophilic colloid layer such as gelatin, PVA, PVP or the like, containing a diffusible oxidizing agent such as ammonium or potassium persulfate and a conventional hardener, such as formaldehyde, mucochloric acid, or the like.

In processing, the color negative material is exposed to an image and developed in a color developer having a high alkalinity, i.e., a pH between 12.5 and 13. The development causes the oxidation products of the developer to form dye images in the exposed areas to thus immobilize the color formers in these areas as shown at **8**, **9** and **10**, FIGURE 3. The unoxidized color formers due to the high alkalinity of the developer start to diffuse from the sensitive emulsion layer **2**. Excess developer is removed from the negative and layer **4** of the negative is then forced into contact with layer **6** of the receiving sheet. The intimate contact of the negative with the receiving sheet permits the unreacted color formers to diffuse image-wise from layer **2** through layer **3** into layer **4** as shown at **11** and **12**, FIGURE 3. Simultaneously, the oxidizing agent in layer **6** is caused to diffuse into layer **4**. Layer **4** is saturated with developer which is oxidized by the diffused oxidizing agent leading to coupling between the diffused color formers and oxidized developer to produce positive dye images. By peeling the receiving sheet from the negative, layer **4** is physically transferred to the receiving sheet. Dye image formation is therefore localized to layer **4**.

The receiving sheet may be prepared by several alternative procedures. Thus a paper or cellulose acetate support may be coated with gelatin containing potassium or ammonium persulfate (2 grams of persulfate and 50 grams of gelatin) and a conventional hardener such as chromalum, formaldehyde or mucochloric caid. Alternatively 10 mls. of 6% gelatin saturated with potassium persulfate is dispersed in 30 mls. of ethyl cellulose in toluene. Ten mls. of this dispersion is then dispersed in 30 mls. of 6% gelatin and coated on the support **5**.

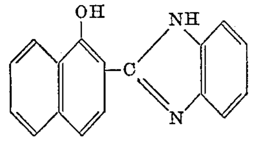
Finally 10 mls. of 6% gelatin are saturated with potassium persulfate and dispersed in 30 mls. of a solution of ethyl cellulose in toluene. 10 mls. of this composition were dispersed in 30 mls. of a composition of 2 grs. of potassium persulfate in 50 grams of 6% gelatin. The composition was coated on support **5**.

The developer which will be employed will be one containing a conventional color developer such as a p-phenylenediamine, i.e., N-ethyl-N-beta-hydroxyethyl-p-phenylenediamine, 2-amino-5-diethylamino toluene, or the like. The developer in addition to the developing agent will contain a perservative, such as sodium sulfite, a restrainer such as potassium bromide, a calcium precipitant, if desired, such as sodium hexametaphosphate, and an alkali designed to give the necessary pH, such as sodium hydroxide, sodium carbonate, or the like.

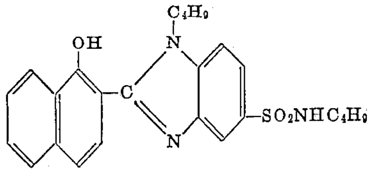
The prerequisites that the special color formers contemplated for use herein must possess have been indicated above. These color formers and their methods of preparation are illustrated in application Ser. No. 279,033

filed Apr. 25, 1963, to which attention is directed. Examples of such color formers are, for instance,

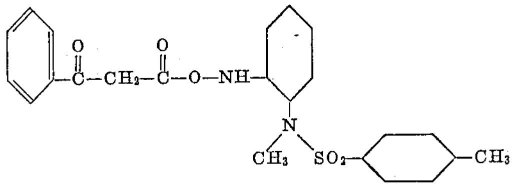
(1)



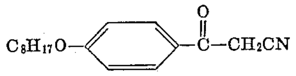
(2)



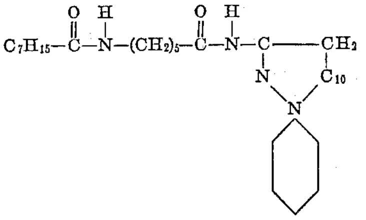
(3)



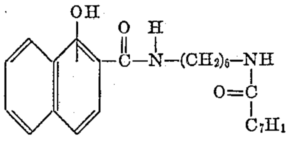
(4)



(5)

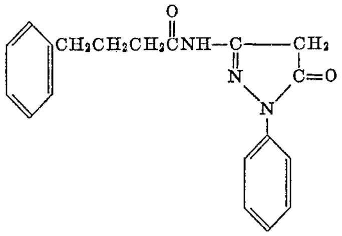


(6)



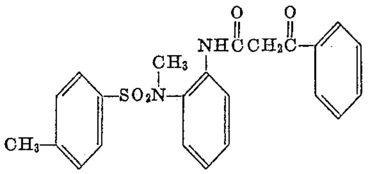
Other suitable color formers are the following:

(7)



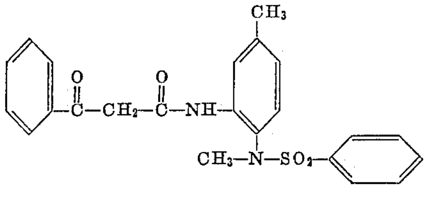
1-phenyl-3-(4-phenybutyrlamido)-5-pyrazolone

(8)

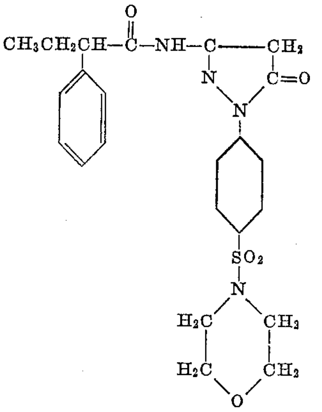


1 - benzoylacetamido-2-(N - methyl - p - toluenesulfonamido)-benzene

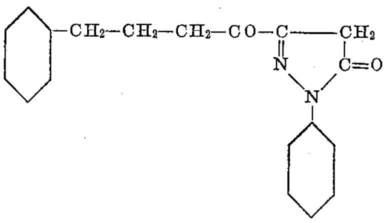
(9)



3 - benzoylacetamido - 4 - (N - methylbenzenesulfonamido)-toluene



1 - (4 - sulfonmorpholido)-phenyl - 3 - (α-phenyl)-butyrylamido-5-pyrazolone



1 - phenyl - 3 - (4-phenylbutyrylamido)-5-pyrazolone

Compound 7 is prepared as follows:

0.1 mole (16.4 g.) of 4-phenylbutyric acid (M.P. 49–51° C.) is allowed to react overnight with 100 mls. of thionyl chloride at room temperature. The excess thionyl chloride is removed under reduced pressure and the residual crude acid chloride is added dropwise at room temperature to a solution of 0.1 moles of 1-phenyl-3-amino-5-pyrazolone in 100 mls. of dry pyridene. The solution is stirred for 3 hours at room temperature and then poured into ice-HCl. A tan solid precipitates which is removed by filtration and then recrystallized from alcohol. The product is 1-phenyl-3-(4-phenylbutyrylamido)-5-pyrazolone.

Compound 9 was prepared as follows:

107 gr. of p-toluidine was dissolved in 300 mls. of dry pyridine, 176 grs. of benzenesulfonyl chloride was added dropwise with stirring below 20° C. over a 45-minute period. The reaction mixture was stirred for an additional hour, heated on a steam bath for 1 hour and then poured into 450 mls. of concentrated hydrochloric acid and 2000 gr. of ice. An orange oil solidified. It was ground in a Waring Blendor, filtered and washed well with water. The damp cake was crystallized from 1500 mls. of ethanol. The mixture was filtered and washed with cold ethanol and dried to yield 4-benzenesulfonamido-toluene.

186 gr. of 4-benzenesulfonamido-toluene was added in portions to a stirred mixture of 69 mls. of 70% nitric acid in 300 mls. of water at room temperature. The suspended material was heated with stirring on a steam bath. The nitration appears to take place at about 85° C. The reaction mixture was steamed and stirred 1 hour and then chilled in ice. The product is an orange oil which solidifies on cooling. It is filtered, washed well in water and the damp cake crystallized from 100 mls. of methanol to give 3-nitro-4-benzene-sulfonamido-toluene.

172 gr. of 3-nitro-4-benzenesulfonamido - toluene was suspended in 625 mls. of 10% sodium hydroxide. 57 grs. of dimethyl sulfonamide was added in a thin stream while keeping the temperature below 20° C. by means of an ice-bath. The reaction mixture was steamed for 3 hours at room temperature whereupon 100 mls. of 28% ammonium hydrochloride was added and the solution stirred for 30 minutes. The mixture was chilled in ice, filtered and the damp cake was crystallized from 500 mls. of methanol. The product was 3-nitro-4-(N-methyl-benzenesulfonamido)-toluene.

132 gr. (0.432 mole) of 3-nitro-4-(N-methylbenzenesulfonamido)-toluene is added in portions to a refluxing solution of 132 gr. (2.36 moles) of 30 mesh iron in 70 mls. of water, 13 moles of 37% hydrochloric acid and 280 moles of ethanol. The reaction mixture is refluxed for an additional 7 hours and then allowed to stand overnight. The solution is filtered through filter cell and the cake washed with hot ethanol. Upon cooling 3-amino - 4 - (N - methyl-benzenesulfonamido)-toluene crystallizes.

90 gr. (0.326 mole) of 3-amino-4-(N-methylbenzenesulfonamido)-toluene and 63 gr. (0.236 mole) of ethylbenzoyl acetate was dissolved in 400 mls. of dry xylene. Under slow distillation ethanol is removed until a temperature of 136° C. is reached. Xylene is then removed under a vacuum until a heavy oil is obtained. With the aid of a vacuum pump the last traces of xylene and most of the unreacted ethylbenzoyl acetate is removed. The residue solidifies. The yellow solid is pulverized and dissolved in methanol and reprecipitates by ice-water/HCl. A light yellow solid is then recrystallized twice from butanol by allowing recrystallization to take place at room temperature. The product, a white solid, is 3-benzoylacetamido - 4 - (N - methylbenzenesulfonamido)-toluene.

Compound 8 is prepared in the same manner as Compound 9 excepting that the 4-benzenesulfonamido toluene is replaced by p-toluene sulfonamido-benzene.

Compound 10 is prepared as follows:

32.8 gr. of α-phenyl butyric acid was reacted at room temperature with 100 ml. of thionyl chloride and allowed to stand overnight. All excess thionyl chloride was then removed under water aspirator vacuum and the product vacuum distilled. The acid chloride was collected at 70–78° C. and 0.15–1.5 mm. 9.13 gr. of α-phenyl butyryl chloride was added dropwise with stirring to 16.2 gr. of 1-(4′-sulfonmorpholido) - phenyl - 3 - amino-5-pyrazolone in 100 ml. of dry pyridine. The temperature was kept at 5°–10° C., stirred 1 hour at room temperature and then 1½ hours on a steam bath. The reaction mixture was then poured into 130 ml. of 37% HCl and 500 gr. of crushed ice. Brown solid was filtered off and recrystallized from aqueous methanol to give 1-(4′-sulfonmorpholido)-phenyl - 3 - (α - phenyl)-butyrylamido-5-pyrazolone.

Compound 11 is prepared as follows:

0.1 mole of 4-phenylbutyric acid and 100 ml. of thionyl chloride are reacted at room temperature overnight. Excess thionyl chloride is removed under reduced pressure and the residual crude acid chloride is added dropwise at room temperature to a solution of 0.1 mole of 1-phenyl-3-amino-5-pyrazolone in 100 ml. of dry pyridine. The solution is stirred for 3 hours at room temperature and then poured into ice/dilute hydrochloric acid. A tan solid precipitates which is recrystallized from alcohol. The product is 1-phenyl-3-(4-phenylbutyrylamido)-5-pyrazolone.

It is to be particularly pointed out that color formers represented by Compounds 9, 10 and 11 are very superior to color former previously proposed for use in the color transfer process which resorts to the pH dependent diffusion principle. Thus they are inherently capable of improving the quality of the images as well as expediting processing. They were found to overcome the shortcomings of previously recorded special color formers in that

(1) They have far superior solubility characteristics in crystalloidal oils described in Jelley et al., U.S.P. 2,322,027;

(2) They have the least tendency to crystallize out in the photosensitive coating upon aging;

(3) They have improved diffusion charcteristics and the least tendency to diffuse at a pH of 13 or higher.

These color formers not only recommend themselves for use in my processing technique hereof but also in that of application, Ser. No. 279,033, filed April 25, 1963 and in my copending application, Ser. No. 92,017 filed Feb. 27, 1961, now abandoned. These color formers in short have general utility in any color negative material for the diffusion transfer process which uses the pH dependent diffusion principle while insuring particular advantages in their use.

A peculiar characteristic of all the special color formers is that substantially no diffusion thereof occurs during preparation of the sensitized element or during negative color development when effected at a relatively low pH, i.e., 10 to 11.5, a condition which excludes the use of hydrophilic color formers which are soluble in solutions of such low alkalinity. This eliminates those color formers described in U.S.P. 2,186,849. On the other hand, the special color formers become capable of diffusing as soon as the pH of the environment reaches or exceeds 12.5. This eliminates the lipophilic type color formers of high molecular weight presently used in commercial color processes which are not diffusible regardless of the pH. Accordingly, in my procedure the color formers which are not reacted during color development of the negative images become diffusible at a pH of 12.5 to 13; they diffuse image-wise at such high pH into the receiving layer which is in intimate and direct-surface contact with the strippable layer **4** of the negative. The diffusion of the unused couplers is, therefore, controlled not by structural modifications of the color former molecule but by the pH of the surrounding medium coupled with the physical effect of the forceful contact between the receiving sheet and the negative material at the high pH. As noted, the diffused color formers produce a positive dye image in layer **4** of the negative in the presence of the oxidizing agent and unused color developer.

Generally speaking, the quantity of color former used per unit of silver halide is selected in such a way that maximum density in the high-light regions of a subject, or the transparent portions of a pattern, is achieved on exposure of the packet or mixed grain color negative material to the subject, or to the pattern, and color developing such areas to maximum density. Thus, in the areas of exposure yielding maximum density on color development, all of the color former will be used up and none can diffuse to the receiving sheet. In other areas, the unused coupler will be rendered diffusible and through the action of the receivng sheet will be transferred image-wise to layer **4** of the negative. Consequently, where maximum density is achieved in the negative materials, no dye image will form in layer **4**. Dye images will only form in layer **4** to the extent that the coupler remains unreacted after color development of the negative material and the pH at which the color couplers become diffusible. Specifically, it is recommended that the ratio of color formers to silver halide per siliver halide emulsion layer be about 10 millimols of color former to 2–20 grams of silver halide.

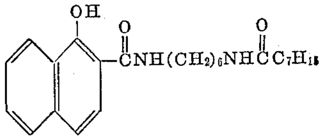
It has been stated above that my procedure may be used with either a mono-layer or multi-layer negative material. When using multi-layer material it is preferred to initiate color development of the negative material for a few minutes, say 2 to 3 minutes, in a color developer having a pH of 10.5 to 11.5 before forcing the negative material into contact with the receiving sheet.

The development is then completed in a developer which has a pH of 12.5 to 13. The low pH developer starts development thus initiating color former immobilization. Diffusion is initiated with the higher pH developer and proceeds at contact of the negative with the receiving sheet.

The invention will be further understood with reference to the following examples, particularly when taken with the drawing:

Example I

A negative mono-layer material as shown in FIGURE 1 is prepared by coating a cellulose triacetate base **1** with a light-sensitive silver halide emulsion layer **2** in which the average size of the oily packets is less than 1 micron. Such coating is produced by dissolving 10 millimols of a cyan color former of the following formula:



in 30 grams of triphenyl phosphate and dispersing the solution by means of a Waring Blendor for 5 minutes in 120 cc. of a 6% aqueous gelatin solution with the addition of .5 cc. of lauryl sulfate 25%. The dispersion is then mixed by hand stirring with 300 grams of a gelatino-silver chloride-bromide emulsion containing 6% of siliver halide and coated on the base with the addition of the usual coating finals. The coating is then dried to form layer **2**, FIGURE 1.

Partition layer **3** is coated on layer **2** as a 5% aqueous solution of gelatin and the coating dried. The partition layer is then overcoated with a 6% aqueous gelatin solution containing mucochloric acid as the hardener and dried to form layer 4 of FIGURE 1.

A receiving sheet, as in FIGURE 2, is prepared by coating a paper base **5** with 50 grams of 6% gelatin containing 2 grams of potassium persulfate and mucochloric acid as the hardener. The coating is then dried to form layer **6**.

The negative is exposed to an image and developed in a developer of the following composition:

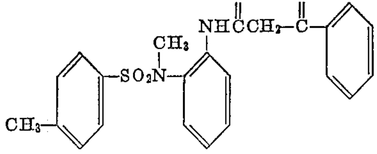
Sodium sulfite	grams	20
Sodium hydroxide	do	15
2-amino-5-diethylamino-toluene	do	4
Sodium bromide	do	2
Water	liter	1

Excess developer is wiped off with a moist sponge and, after 60 seconds, layer **4** of the negative is forced into contact with layer **6** of the transfer sheet as shown in FIGURE 3. Diffusion of the color former from layer **2** and oxidizing agent from layer **6** into layer **4** causes oxidation of the color developer in layer **4** and the reaction thereof with the color former to produce positive dye images. The peeling of the receiving sheet from the negative material causes a physical transfer of the strippable hardened layer **4** with the dye images to the receiving sheet.

This procedure avoids subsequent washing and yields dense, stain-free cyan dye images. Control of the diffusion and oxidization is provided by virtue of the physically strippable layer **4** to which dye image formation from diffused color former is localized.

Example II

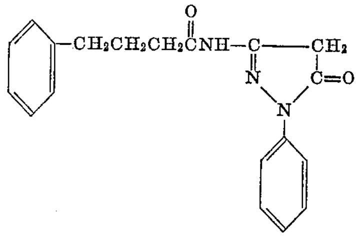
The procedure is the same as in Example I excepting that the sensitized layer of the negative material is produced with the following color former:



Dense, stain free, yellow images were formed in the strippable layer **4**.

Example III

The procedure is the same as in Example I excepting that in producing the negative material, there is used the magenta color former of the following constitution:



Magenta images of excellent quality were formed in layer 4.

Example IV

This example illustrates a negative material containing three superimposed silver halide emulsions containing a different color former, each layer sensitized to a primary color. A baryta-treated paper base is coated with the silver halide emulsion of Example I in which the emulsion is sensitized with a conventional red sensitizer. Upon the red sensitized layer is applied a green sensitive layer described in Example III but wherein the silver halide is sensitized with a sensitizer of the type described in U.S.P. 2,295,276. On top of the green sensitized layer is applied a 3% gelatin separating layer containing yellow colloidal silver as a filter layer. On top of the filter layer is coated the silver halide emulsion of Example II. The outermost layer is then coated with the partition layer 3 which is in turn overcoated with the hardened strippable gelatin layer 4.

The negative was exposed and developed for 5 minutes at 25° C. in a solution of the following composition:

2-amino-5-diethylamino-toluene	grams	4
Sodium sulfite	do	10
Borax	do	5
Sodium hydroxide	do	1.5
Benzyl alcohol	cc	3
Sodium bromide	gram	.5
Water	liter	1

The developed image was then brought into contact with layer 6 of the receiving sheet in the presence of the following high pH developer:

2-amino-5-diethylamino-toluene	grams	4
Sodium sulfite	do	20
Sodium hydroxide	do	15
Sodium bromide	do	2.5
Water	liter	1

Upon peeling the receiving sheet from the negative, the adhering layer 4 will be found to contain three color dye images which are dense and stain free.

Example V

The procedure is the same as in Example I excepting that the color former is 1 - phenyl-3 - (4 - phenylbutyrylamido)-5-pyrazolone. The transferred image is of excellent quality and lends itself very readily to the involved processing.

Example VI

The process is the same as in Example I excepting that the color former employed is 1-(4′-sulfonmorpholidophenyl-3-(α-phenyl)butyrylamido)-5 - pyrazolone. Dense magenta images are obtained in layer 4.

Example VII

The process is the same as in Example I excepting the color former employed is 3-benzoylacetamido-4-(N-methylbenzenesulfonamido)-toluene. Layer 4 when transferred to the receiving sheet contains dense, stain free yellow images.

Modifications of the invention will occur to persons skilled in the art and I therefore do not intend to be limited in the patent granted except as necessitated by the appended claims.

I claim:

1. A process for producing a dye image on an unsensitized receiving sheet which comprises exposing to light a photographic negative comprising a silver halide emulsion overcoated with a hardened, strippable, hydrophilic colloid coating, said emulsion having dispersed therein oily packets containing a color former, said oily packets being produced by dissolving the color former in a substantially water insoluble, low molecular weight, organic crystalloidal material having a boiling point above about 175° C., said crystalloidal material having a high solvent action for the color former and for the dye formed therefrom and being permeable to photographic processing solutions, the nature and proportions of the color former and crystalloidal material being so chosen that particles thereof are liquid under conditions of coating and processing the emulsion, said color former being capable of reacting with the oxidation products of a primary aromatic amino color developer to produce a non-diffusible dyestuff image selected from the class consisting of a quinoneimine and azomethine dye image, said color former being free from water solubilizing groups but sufficiently soluble in the aforesaid crystalloidal material as to be incorporated in an oily packet and containing such organic groups that at a pH of at least as high as 12.5, the color former becomes diffusible in an aqueous medium, the exposure being sufficient to ensure maximum density in the emulsion upon color development of those areas in the emulsion corresponding to the high-light areas of the subject to be reproduced, color developing the emulsion in a primary aromatic amino developer having a pH as high as 12.5 to produce such maximum density with complete conversion and immobilization of the color former in the areas of maximum density to a non-diffusible dye image, providing a receiving sheet comprising a base coated with a hydrophilic colloid containing a diffusible oxidizing agent, pressing the hardened, strippable coating on the silver halide emulsion into contact with the hydrophilic colloid of said receiving sheet to cause image-wise diffusion of the color former from the emulsion into said hardened, strippable coating and the oxidizing agent from the hydrophilic colloid on said receiving sheet into said hardened, strippable coating, oxidizing the color developer in the hardened, strippable coating by said oxidizing agent, reacting the oxidized developer with diffused color former in said hardened, strippable coating to produce a dye image therein and peeling the receiving sheet from the negative with the hardened, strippable coating adhering to said receiving sheet.

2. The process as defined in claim 1 wherein a partition layer of a soft hydrophilic colloid is interpolated between the emulsion layer and the hardened, strippable coating to expedite the transfer of said coating to said receiving sheet.

3. The process as defined in claim 1 wherein color development is initiated at a pH below 12.5 and is completed at a pH at least as high as 12.5.

4. The process as defined in claim 1 wherein the negative contains three superimposed emulsion layers, the innermost being sensitive to red and containing a cyan color former, the intermediate being sensitive to green and containing a magenta color former and the outermost being sensitive to blue and containing a yellow color former.

5. The process as defined in claim 4 wherein color development is initiated with a color developer at a pH below 12.5 and is completed with a color developer at a pH at least as high as 12.5.

6. A negative silver halide material for the diffusion transfer process comprising a base coated with a silver halide emulsion having dispersed therein oily packets con-

taining a color former selected from the class consisting of 1-(4'-sulfonmorpholido)-phenyl-3-(α-phenyl)-butyrylamido-5-pyrazolone, 1-phenyl-3-(4-phenylbutyrylamido)-5-pyrazolone and 3-benzoylacetamido-4-(N-methylbenzenesulfonamido)-toluene, said oily packets being produced by dissolving the color former in a substantially water insoluble, low molecular weight, organic crystalloidal material having a boiling point above about 175° C., said crystalloidal material having a high solvent action for the color former and for the dye formed therefrom and being permeable to photographic processing solutions, the proportion of the color former and crystalloidal material being so chosen that particles thereof are liquid under conditions of coating and processing the emulsion.

7. The article as defined in claim **6** wherein the silver halide emulsion is overcoated with a hardened, strippable layer of a hydrophilic colloid.

8. A process for producing a dye image of an unsensitized receiving sheet which comprises exposing to light a photographic negative comprising a silver halide emulsion overcoated with a hardened, strippable, hydrophilic colloid coating, said emulsion having dispersed therein oily packets containing a color former selected from the group consisting of 1-phenyl-3-(4-phenylbutyrylamido)-5-pyrazolone, 1-(4'-sulfonmorpholido)-phenyl-3-(α-phenyl)-butyrylamido-5-pyrazolone and 3-benzoylacetamido-4-(N-methylbenzenesulfonamido)-toluene, said oily packets being produced by dissolving the color former in a substantially water insoluble, low molecular weight, organic crystalloidal material having a boiling point above about 175° C., said crystalloidal material having a high solvent action for the color former and for the dye formed therefrom and being permeable to photographic processing solutions, the nature and proportions of the color former and crystalloidal material being so chosen that particles thereof are liquid under conditions of coating and processing the emulsion, said color former being capable of reacting with the oxidation products of a primary aromatic amino color developer to produce a non-diffusible dyestuffs image selected from the class consisting of a quinoneimine and azomethine dye image, said color former being free from water solubilizing groups but sufficiently soluble in the aforesaid crystalloidal material as to be incorporated in an oily packet and containing such organic groups that at a pH of at least as high as 12.5, the color former becomes diffusible in an aqueous medium, the exposure being sufficient to ensure maximum density in the emulsion upon color development of those areas in the emulsion corresponding to the high-light areas of the subject to be reproduced, color developing the emulsion in a primary aromatic amino developer having a pH as high as 12.5 to produce such maximum density with complete conversion and immobilization of the color former in the areas of maximum density to a non-diffusible dye image, providing a receiving sheet comprising a base coated with a hydrophilic colloid containing a diffusible oxidizing agent, pressing the hardened, strippable coating on the silver halide emulsion into contact with the hydrophilic colloid of said receiving sheet to cause image-wise diffusion of the color former from the emulsion into said hardened, strippable coating and the oxidizing agent from the hydrophilic colloid on said receiving sheet into said hardened, strippable coating, oxidizing the color developer in the hardened, strippable coating by said oxidizing agent, reacting the oxidized developer with diffused color former in said hardened, strippable coating to produce a dye image therein and peeling the receiving sheet from the negative with the hardened, strippable coating adhering to said receiving sheet.

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Disclaimer

3,359,104.—*Felix Viro,* Apalachin, N.Y. COLOR DIFFUSION TRANSFER PROCESS AND NEGATIVE MATERIAL THEREOF. Patent dated Dec. 19, 1967. Disclaimer filed Sept. 30, 1982, by the assignee, *Eastman Kodak Co.*

Hereby enters this disclaimer to all claims of said patent.

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