

- [54] **COLOR DIFFUSION TRANSFER PROCESS UTILIZING AZO COUPLING TO ACTUATE DIFFUSION OF COLOR PROVIDING SPECIES**
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- [73] Assignee: **GAF Corporation**, New York, N.Y.
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- [52] U.S. Cl. **96/3, 96/29 D, 96/77**
- [51] Int. Cl. **G03c 7/00, G03c 1/00, G03c 1/40**
- [58] Field of Search..... **96/3, 77, 29 D**

[56] **References Cited**

UNITED STATES PATENTS			
3,065,074	11/1962	Rogers.....	96/3
3,301,772	1/1967	Viro.....	96/3
3,359,104	12/1967	Viro.....	96/3
3,676,124	7/1972	Ohkubo et al.	96/3

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Assistant Examiner—Richard L. Schilling
Attorney, Agent, or Firm—Walter C. Kehm; Samson B. Leavitt

[57] **ABSTRACT**

In a color diffusion transfer process utilizing azo coupling as a means to actuate solubilization and to accelerate the diffusion transfer process of color providing species, light sensitive layers are provided which contain oil dispersions of 4-equivalent color formers capable of coupling in the alkaline processing solution with the oxidation product of a p-phenylene diamine color developer and thereby form imagewise non-diffusible and insoluble dye species. These color formers are also capable of reacting with incorporated highly diffusible carboxy or sulfo substituted diazonium salts or their precursors to yield alkali soluble and highly diffusible azo dyes which diffuse imagewise to a mordanted receiving layer. In the receiving layer a p-phenylene diamine developer is oxidized for the purpose of converting these azo dyes via oxidative coupling into azo methine or indoaniline dye species thereby providing a true reproduction in color, hue and density of the scene originally recorded in the light sensitive silver halide layers.

13 Claims, 10 Drawing Figures

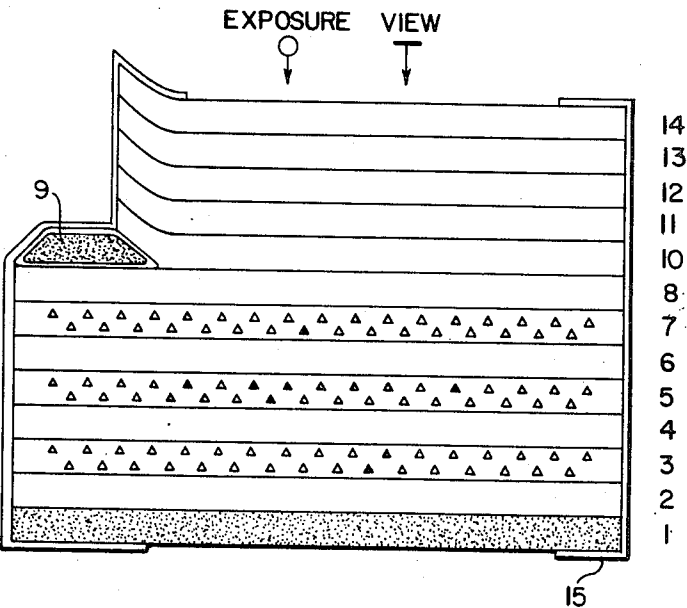


FIG. 1

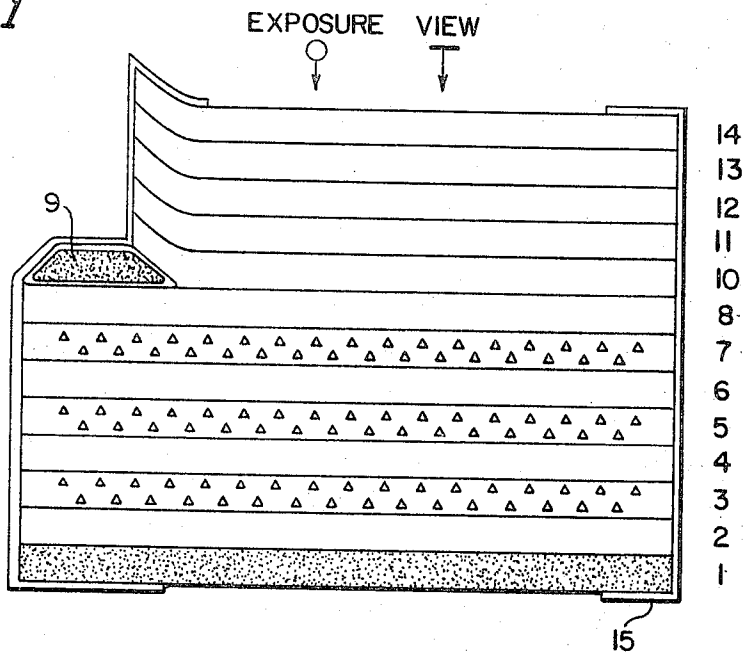
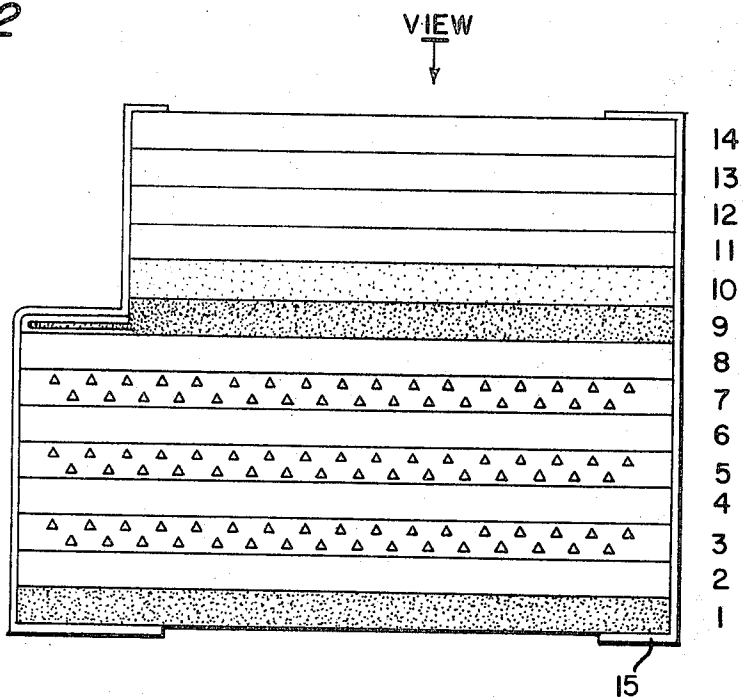


FIG. 2



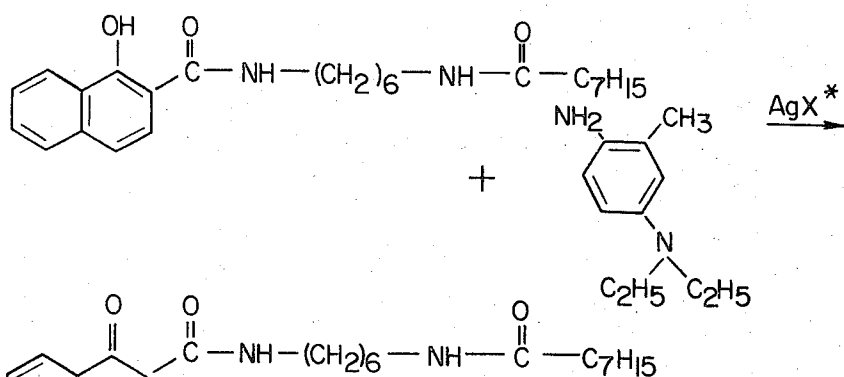


FIG. 3a

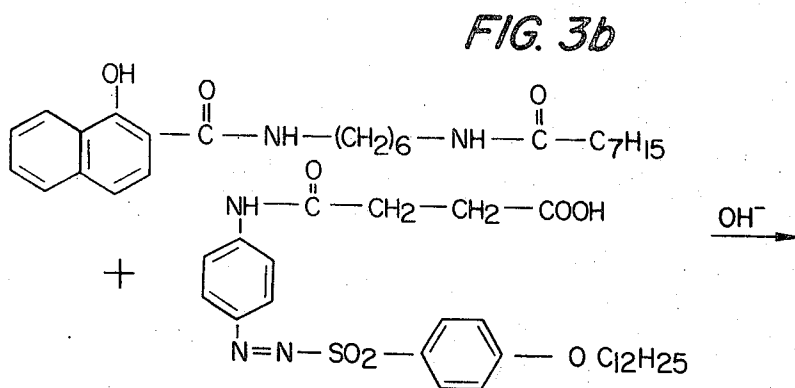
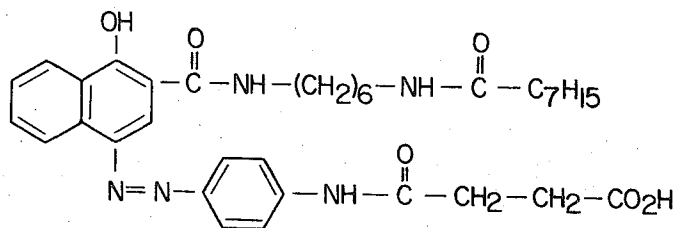


FIG. 3b



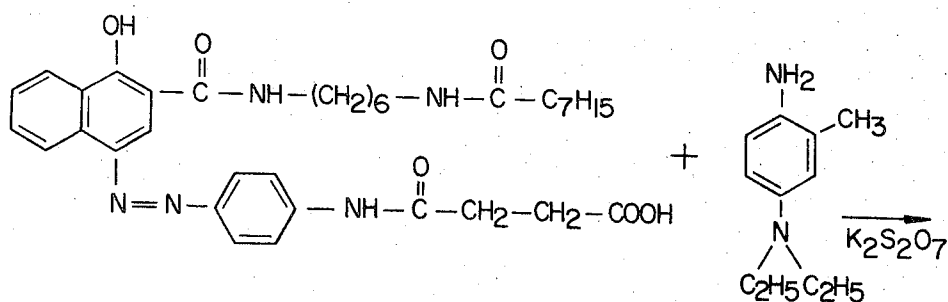


FIG. 3c

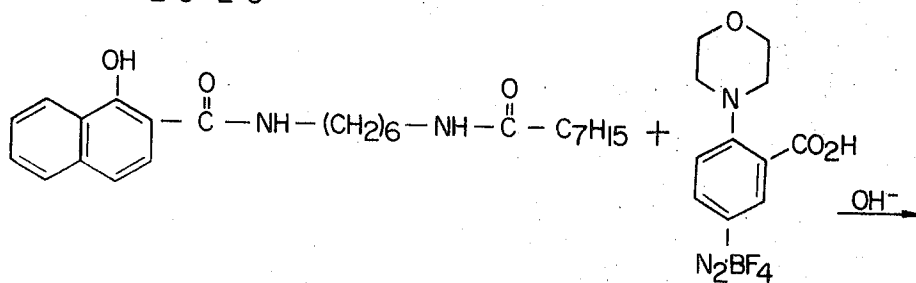


FIG. 3d

FIG. 5

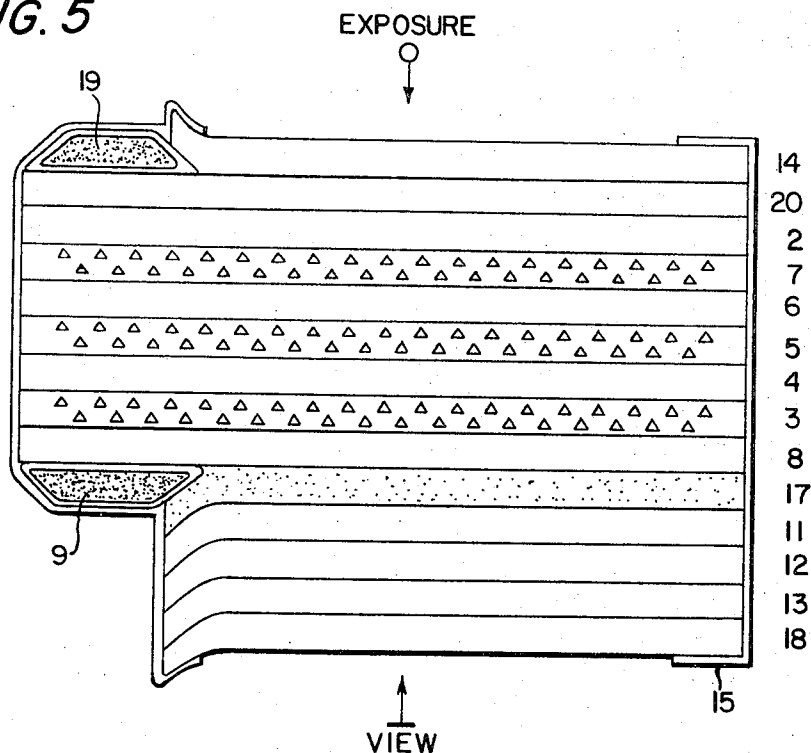


FIG. 4

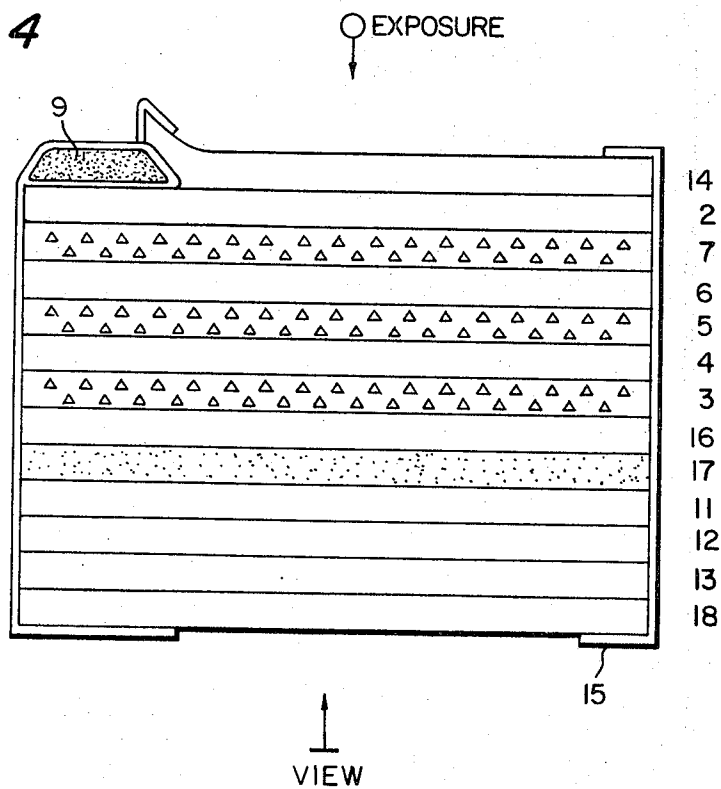
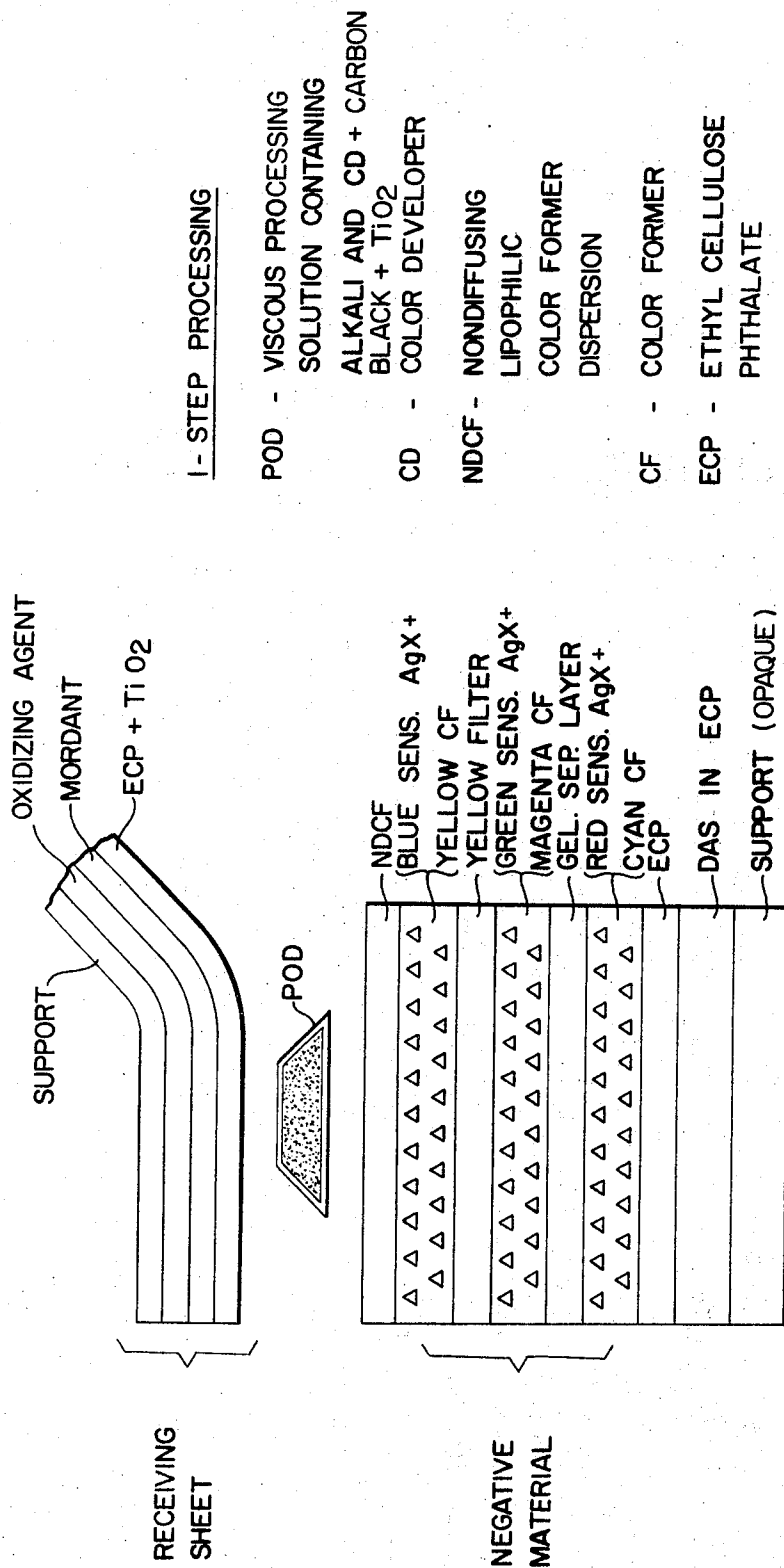


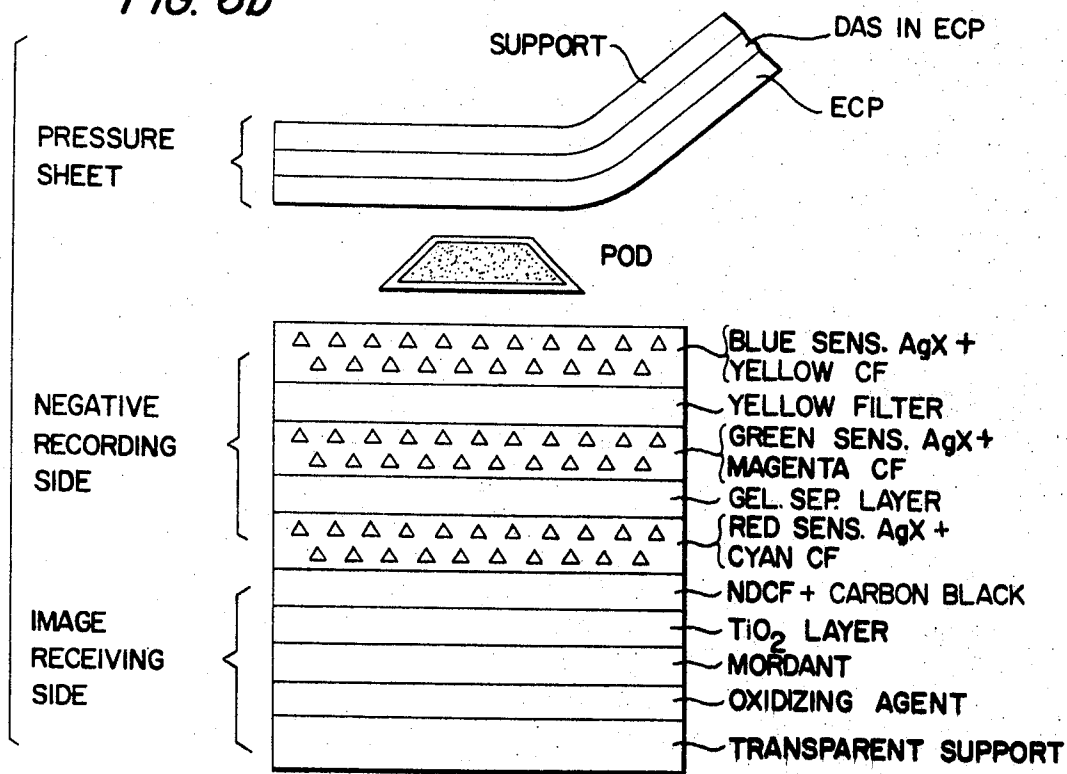
FIG. 6a



I-STEP PROCESSING

- POD - VISCOUS PROCESSING SOLUTION CONTAINING ALKALI AND CD + CARBON BLACK + TiO2
- CD - COLOR DEVELOPER
- NDCF - NONDIFFUSING LIPOPHILIC COLOR FORMER DISPERSION
- CF - COLOR FORMER
- ECP - ETHYL CELLULOSE PHTHALATE
- DAS - DIAZONIUM SALT

FIG. 6b



COLOR DIFFUSION TRANSFER PROCESS UTILIZING AZO COUPLING TO ACTUATE DIFFUSION OF COLOR PROVIDING SPECIES

BACKGROUND OF THE INVENTION

1. Field of the Invention

The invention relates generally to a method of obtaining color reversal transfer images with negative emulsion systems utilizing azo dye formation as the solubilizing transport mechanism of the system.

2. Description of the Prior Art

The broad use of azo dyes in a multi-color diffusion reversal transfer process is not by itself a novel method, see British Pat. No. 1157505 to Ilford Limited and Renfrew U.S. Pat. No. 3,329,590, nor is the solubilization by reacting azo dyes with oxidized p-phenylene diamine in exposed imagewise areas a new method. Oxidative decoupling is taught in Barr, U.S. Pat. No. 3,227,551. In all of these cases of the prior art an azo dye is either the original color former or the end product imaging dye as in British Pat. No. 804,976. In the present proposed system of the invention, the use of a diazonium salt, in the proper timing sequence, effects diffusion transfer from an already imaged or imaging silver halide layer, and the resulting azo dyes are employed *only* as the means of transporting color formers. The azo dyes are mordanted onto the receiving sheet until enough oxidized p-phenylene diamine is formed to convert the azo dyes to azomethine or indo-aniline dyes.

SUMMARY OF THE INVENTION

A positive multi-color diffusion product is constructed by coating a negative film package of blue, green, and red sensitive emulsion layers containing 4-equivalent yellow, magenta and cyan oil soluble color formers, respectively and diazonium salts or diazonium precursors which give mobility to the color formers.

In a preferred embodiment the diazonium salt or its precursor may be placed behind a polymeric timing layer to thereby delay the diffusion of the color providing species until development has proceeded substantially to completion. This permits an added measure of control over earlier color former based color transfer processes (see U.S. Pat. Nos. 2,661,293 and 2,647,049).

In another form of the invention non-diffusing diazonium precursors are placed between the emulsion layers to couple with the 4-equivalent couplers which are themselves slightly soluble and diffusible at the operating or development pH to generate highly diffusible species.

The diazonium salts or their precursors may also be placed within the emulsion layers forming the highly diffusible azo species upon alkaline treatment (i.e., when subjected to the developer solution). This is an improvement over the alkali actuated diffusion process of the prior art inasmuch as preceding color formers were mobilized either by ionization (thus generating a much slower moving species) or by utilization of carboxylic or sulfo groups with like color formers (which endowed them with a certain degree of diffusibility even at neutral pH and thus a hindrance during coating). (See U.S. Pat. Nos. 2,661,293, 2,647,049, 2,661,293 and 3,359,104).

The use of carboxy or sulfo diazonium salts has the additional benefit of permitting the mordanting of the diffusing azo species whereas diffusing color formers as in U.S. Pat. No. 3,301,772 are not so fortunately endowed.

In the operation of the invention, exposure is followed by treatment with an alkaline processing solution containing a N,N-dialkyl substituted paraphenylene diamine which reduces the exposed silver halide grains and couples with either the color formers or azo dyes, insolubilizing them, thereby leaving an imagewise distribution of soluble dye providing species. The flow of such species is facilitated by a mordanting sink action in the positive or receiving portion of the film package where application of an oxidizing agent or the use of incorporated oxidizing agent or other methods of generating oxidized developer (see U.S. Pat. No. 3,301,772) converts the azo dye to an indoaniline or azomethine dye thereby rendering the recorded original scene faithful in regards to hue, color and density variations.

The advantages of using diazonium salt actuated diffusion are at once obvious in view of the accelerated flow and sink action and thus constitute an improvement to the existing art in photography.

By the use of diazonium salts or their precursors the line of distinction between mobile and immobile color providing species becomes easy to regulate. As in prior art processes (see U.S. Pat. Nos. 3,301,772 and 3,359,104), the use of alkali to generate diffusible species requires ionization of the color formers involved which is an imprecise and cumbersome method of solubilization. The former method also has the disadvantage of producing slowly diffusible species and limits the selection of color formers to those which are essentially immobile at the development pH but diffusible at a higher pH. Furthermore, the mechanism of raising the pH within a given period of time is unavoidably complex. Last of all, neutralization of this alkali in the final film package, to generate a stable dye image, requires more stringent methods than that necessary within the scope of the present invention, as anyone skilled in the art can plainly see.

The existence of an azo dye rather than a 4-equivalent color former also has the benefit of reducing the requirements of oxidizing agents incorporated into the receiving sheet, for conversion, to one-half that of prior art systems since the formed azo dyes act as 2-equivalent couplers. (See Chapter 17, Mees, *The Theory of the Photographic Process*, Third Ed., 1966).

By using color formers in any of the three embodiments detailed above, the rate of diffusion is readily regulated by virtue of the placement of carboxy, sulfo or any number of these groups upon the diffusion actuating species. Thus, as in the case of the preferred embodiment the mobilizing species may be made to be extremely diffusing and hence upon introduction of the diazonium salt or its precursor at a given point (predetermined by the delay, provided by the timing layer) an almost instantaneous coupling reaction ensues providing a mobilization of the color providing species which is so rapid that further modulation of the azo dye is almost impossible and hence misinformation referred to in the art as "cross-talk" is avoided.

DESCRIPTION OF THE PREFERRED EMBODIMENT

The inclusion of the diazonium compound as a salt, a stabilized metal complex, or as a diazonium precursor such as an azo sulfone (all of which are well-known in the art) is an advancement of the art due to the greater mobility during transfer and the greater selection of 4-equivalent color formers available to the practitioner of this invention. A preferred embodiment suggests the use of a delaying mechanism to effect transfer in order to provide time for complete development of the negative image.

As a first preferred embodiment use is made of a diazonium salt or preferably an azosulfone which is both soluble and diffusible at the processing pH either encapsulated or incorporated behind a timing layer. This timing layer may be any of a number of alkali degradable or soluble or permeable polymers which will permit a time lag between initiation of development and diffusion of the diazonium species through the negative. As an example but in no way a limitation to this patent is the half butyl ester of maleic anhydride methyl vinyl ether copolymer which when coated to a thickness of 1.5μ offers a delay of about 50 seconds at pH 11.5 before becoming permeable to the incorporated diazonium species.

Upon introduction of a buffered alkaline processing solution containing a N,N-dialkyl paraphenylene diamine (such as 4-N,N-diethylamino-2-methyl aniline) with the appropriate development accelerators (such as metol and phenidone), and a film forming thickening agent (such as carboxy methyl cellulose) the exposed light sensitive portion of the package undergoes negative development resulting in an imagewise distribution of non-diffusible and unreactive azomethine or indoaniline dyes (corresponding to light struck areas) and 4-equivalent color formers (corresponding to unexposed portions of the film). After a given period of time (between 30-60 seconds) full development has been effected and the diazonium species are released from behind their timing layer to flow through the negative portion of the package, reacting with the left-over couplers, to form an imagewise distribution of diffusible 2-equivalent couplers as azo dyes. These species are then pulled in a sink fashion to the receiving portions of the film where they are mordanted and converted to azomethine or indoaniline dyes by virtue of oxidative coupling with oxidized N,N-dialkylparaphenylene diamine (either initially incorporated within the receiving layers or as part of that which was furnished from the processing solution) and oxidizing agent (either provided in the receiving layers as an incorporated species or supplied by virtue of a post-transfer processing step, or created electrolytically) (see for example U.S. Pat. No. 3,301,772).

The color formers utilized within this embodiment are preferably oil soluble and essentially non-diffusible at the development pH but must be capable of diffusion after azo coupling. As examples of those color formers which may be employed within the scope of the first embodiment are those listed in U.S. Pat. No. 3,369,104 which when the processing solution is kept at pH 11.5 or below are essentially immobile. As examples but again in no way a limitation to the scope of this patent are the diazonium salt and the diazonium sulfone 3-carboxy-4(1-pyrrolidinyl)benzenediazonium fluoborate

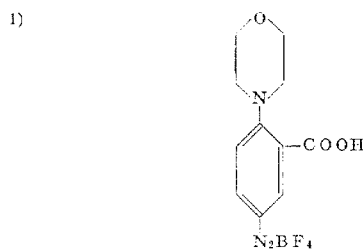
rate and 5-phenylsulfonylazo-2(1-pyrrolidinyl) benzoic acid.

As a second preferred embodiment is the utilization of non-diffusing azo-sulfones which are incorporated in the negative between the emulsion layers. These species have the general formula of SOL-DIAZ-LINK-MORD where SOL refers to any number of solubilizing groups, DIAZ is the diazonium portion of the molecule, LINK is a fragmentable function which binds the SOL-DIAZ to the mordanting portion of the molecule (MORD) but which cleaves from the DIAZ portion upon reaction with the 4-equivalent color formers, and MORD is any number of polymeric or long chain alkyl substituents which renders the diazonium precursor non-diffusible. As an example, but in no way limitative to this patent, is N-(p-(dodecyloxyphenylsulfonylazo)phenyl)-succinamic acid as a useful diazosulfone to be employed within this preferred embodiment.

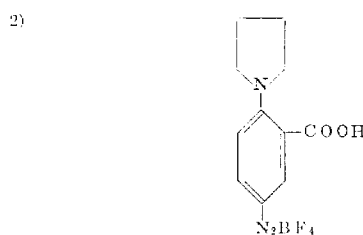
As examples of color formers to be employed are those listed in U.S. Pat. No. 3,369,104 which, when the processing pH is rendered high enough (pH 11.5 - 13.0) achieve some degree of diffusibility, permitting them to transfer to an adjacent layer, due to the sink action of the reaction providing azo-sulfone.

Upon introduction of a buffered alkaline solution containing a paraphenylene diamine developer, development accelerators and a film forming thickening agent, all of which are similar to those of the first preferred embodiment, imagewise formation of dye is produced by imagewise formation of oxidized developer. Concurrent with this reaction is the diffusion of unreacted couplers to the adjacent azo-sulfone bearing layers where azo formation and a higher order of mobility is imparted to the color providing species. The following steps, after azo formation occurs, are the same as those of the first preferred embodiment.

As examples of diazonium salts or azosulfones which may be employed within the scope of the invention, mention may be made of the following:



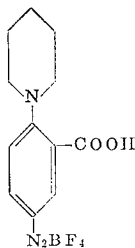
3-carboxy-4-morpholinobenzenediazonium fluoborate



3-carboxy-4(1-pyrrolidinyl)benzenediazonium fluoborate

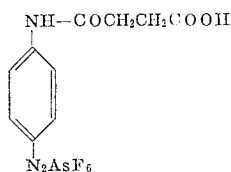
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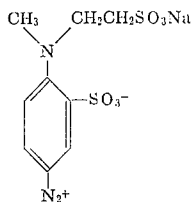


3-carboxy-4-piperidinobenzenediazonium fluoborate

4. 4(3-carboxypropionamido)benzenediazonium hexafluoroarsenate

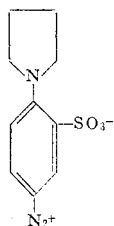


5)



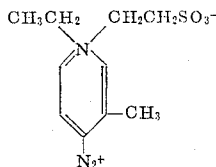
4-[methyl(2-sulfoethyl)amino]3-sulfobenzenediazonium inner salt

6)



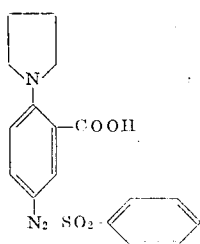
4(1-pyrrolidinyl)3-sulfobenzenediazonium inner salt

7)



4-[ethyl(2-sulfoethyl)amino]o-toluene-diazonium inner salt

8)

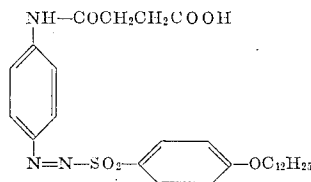


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5-phenylsulfonylazo-2(1-pyrrolidinyl)benzoic acid

9)

5



10

N-[p-(p-Dodecyloxyphenylsulfonylazo)phenyl]succinamide acid

BRIEF DESCRIPTION OF THE DRAWINGS

FIGS. 1, 4, and 5 are diagrammatic enlarged cross-sectional views of three non-peel apart film units embodying the invention.

FIG. 2 is a diagrammatic cross-section of FIG. 1 after exposure has taken place and the film unit has been subjected to roller application.

FIGS. 3, a, b, c, d are descriptive formula of the reactions of negative development, azo dye formation employing azo-sulfones, indoaniline dye formation and azo dye formation employing a diazonium salt.

FIG. 6a is a diagrammatic enlarged cross-section of a film unit emphasizing the use of timing layers and receiving sheet.

FIG. 6b is a diagrammatic enlarged cross-section of a non-peel apart two-piece package employing a pressure sheet containing diffusible diazonium species behind a timing layer.

DETAILED DESCRIPTION OF THE INVENTION

Oxidative coupling between N,N-dialkylparaphenylene diamines and color formers, whether 4-equivalent or as their 2-equivalent azo derivatives, is well known and amply described in *The Theory of the Photographic Process*, Chapter 17, Third Ed. (1966) by Mees. Reactions between diazonium salts or azo sulfones and various couplers are also well documented as described in *The Chemistry of the Carbon-Nitrogen Double Bond*, Chapter 2, Ed. by Saul Patai (1970), and U.S. Pat. No. 3,661,573. The employment of the former as a method of image formation along with the latter as a means of diffusion actuation is unique, however.

The combination of both of these mechanisms permits the use of colorless, color providing species within the emulsion layers, and hence a diversity not readily afforded to most other color transfer processes is available, whereby a multitude of layer arrangements and package configuration is possible.

The following examples serve as illustrations as to the possible employments of our invention and to facilitate the teaching of the concepts described therein. They should not be accepted as the only arrangement possible by which the invention may be employed as variations of package construction are obvious to those skilled in the art. Neither should the suggested employment of specific opacifying agents, reflective agents or the like be construed to limit the scope of the invention as equivalent substitutions are readily obvious to those skilled in the art and are omitted for the sake of brevity and a clearer description of the teachings of the invention.

FIGS. 1 and 2 exemplify one preferred means by which the invention may be practiced. The layers of

FIGS. 1 and 2 embody the conceptual employment of non-diffusing diazonium precursors placed in the gelatin separation layers between the light sensitive layers. The diagrammatic cross-section of FIG. 2 describes the film package as shown in FIG. 1 after it has been subjected to roller application and the processing solution described in layer 9 has been extruded between layers 8 and 10. As shown in FIG. 1, exposure and final viewing of the finished print occurs from the same side. The package therefore is most aptly employed in an imaging system referred to as Lateral Reversal corrected, see E. H. Land, *Photogr. Sci. Eng.*, 16, 247 (1972).

Layer 1 of FIG. 1 is an opaque diazosulfone pigmented film base such as polyester, polycarbonate, cellulose acetate, cellulose acetate butyrate and the like with a thickness of $2\frac{1}{2}$ to 9 mils. It serves the dual function of a support as well as a barrier to unwanted exposure by virtue of an opacifying agent such as carbon black, titanium dioxide, combinations of same or the like which is constructed as part of the base or coated upon the base. Layer 2 is a gelatin matrix layer containing a non-diffusing diazonium precursor such as a diazosulfone which is capable of reacting with 4-equivalent color formers under alkaline conditions forming alkali soluble and highly diffusible azo dyes.

Layer 3 is a red-light-sensitive silver halide emulsion layer containing an oil dispersion of cyan 4-equivalent color former which becomes only moderately diffusible under the influence of the alkaline processing solution, but which forms a highly mobile azo dye with the diffusion actuating diazonium precursor.

Layer 4 is a gelatin separation layer of the same composition as layer 2.

Layer 5 is a green-light sensitive silver halide emulsion layer containing an oil dispersion of magenta 4-equivalent color former which behaves as the cyan component in layer 3.

Layer 6 is a gelatin matrix layer containing a non-diffusing diazonium precursor such as a diazosulfone as in layers 2 and 4 and a blue light absorbing species such as yellow colloidal silver which prevents blue light from reaching layers 3 and 5.

Layer 7 is a blue-light-sensitive silver halide emulsion layer containing an oil dispersion of 4-equivalent yellow color former which behaves as the cyan and magenta color formers of layers 3 and 5.

Layer 8 is a gelatin matrix layer containing a non-diffusing 4-equivalent color former or any such species which will react with any amount of diazonium salt that might be produced after processing has been completed. The product thus produced will not be diffusible and hence no image degradation will occur.

Layer 9 is a pressure rupturable processing pod containing a p-phenylene diamine developer, an antioxidant, alkali, a film forming thickening agent, and opacifying agent such as TiO_2 or the like along with auxiliary light blocking or absorbing agent such as carbon black, non-diffusible dyes, or the like in sufficient concentration as to assure full development of all silver halide in fully exposed regions and to protect the negative portion of the film from further exposure when removed from the camera.

Layer 10 is a gelatin matrix layer containing a reflective species or its precursor which by virtue of its coated form or its concentration or the layer thickness is relatively transparent to actinic radiation but subsequent to application of the processing solution be-

comes opaque enough to act as a visual barrier to the auxiliary opacifying agent of the pod. As an example, but in no way a limitation, is titanium dioxide coated at a 10 percent concentration in 6 percent gel solution whereby the particle size prior to processing is of a mean average size less than 0.05μ , but after processing a mean average size due to coagulation of 0.5μ or greater.

Layer 11 is a mordanting receiving layer of acid treated gelatin and acid mordanting polymeric or non-diffusing basic substances such as amino guanidine derivatives.

Layer 12 is a polymeric timing layer such as polyvinyl alcohol or the like as listed in U.S. Pat. No. 3,455,686 and containing encapsulated oxidizing agents, such as potassium persulfate.

Layer 13 is a pH lowering layer composed of or containing polymeric acids or anhydrides as listed in U.S. Pat. No. 3,362,819.

Layer 14 is a transparent film base such as polyester, polycarbonate, cellulose acetate, cellulose acetate butyrate and the like with a thickness of $2\frac{1}{2}$ to 9 mils.

Layer 15 is a pressure sensitive tape as a binder to hold the negative element permanently bound to the image receiving element and the processing pod.

Subsequent to exposure the package as shown in FIG. 1 is either manually or mechanically forced between rollers which extrude the contents of the pod thereby forming layer 9 as shown in FIG. 2. Upon introduction of the processing solution, development proceeds as chemically visualized for the cyan layer in FIG. 3a. In unexposed regions, the color formers of layers 3, 5, 7 which are themselves soluble and slightly diffusible at the processing pH, are pulled in a sink fashion to the diazosulfone bearing layers of 2, 4 and 6 in which the reactions of azo formation depicted in FIG. 3b for layer 2 proceeds. The azo dyes thus generated migrate to the receiving portion of the package (layer 11) where they are mordanted and then converted to the appropriate indoaniline or azomethine dyes by virtue of oxidative cleavage and coupling with oxidized paraphenylenediamine as shown in FIG. 3c.

FIGS. 4 and 5 are further illustrative examples of layer arrangements to be employed in the practice of the invention. Unlike in FIGS. 1 and 2, exposure and viewing take place at opposite portions of the film package and hence laterally reversed cameras which are the design most often utilized in the photographic field, may be employed in conjunction with these layer arrangements. It is important to note that only with colorless color providing material may both such constructions exist, and hence employment of the invention and the configurations described above and below offers an advancement of the art to the practice of instant access color photography with regards to the selection of image recording devices to be employed.

FIG. 4 employs a single pod construction of a non-peel-apart package, while FIG. 5 employs a double pod construction. The layers of FIGS. 4 and 5 may be defined as:

Layers 2 through 15 are described as above for FIGS. 1 and 2;

Layer 16 is a gelatin matrix layer containing a non-diffusing 4-equivalent coupler as described in layer 8 plus opacifying agents such as non-diffusing dyes or carbon black or the like to render that portion of the package opaque to unwanted exposure;

Layer 17 is a white opaque pigment light reflective layer of TiO_2 and gelatin;

Layer 18 is as described in layer 14;

Layer 19 is a pressure rupturable pod containing a thickening agent and carbon black in a form of a paste as described in U.S. Pat. No. 3,635,707;

Layer 20 is a support layer as described in layer 14.

Just as the employment of colorless color providing 4-equivalent couplers and non-diffusing diazonium precursors offer a superior degree of diversity as to the layer arrangements which may be utilized, the employment of 4-equivalent color formers and diffusible diazonium salts or precursors when employed with a timing layer also permit the use of either the laterally reversed or laterally reversed corrected optical systems.

FIGS. 6a and 6b employ the laterally reversed corrected and laterally reversed systems respectively. In the employment of the invention as shown in FIGS. 6a and 6b, the negative portion of the film and the pressure sheet or receiving sheet may initially be separate or may be joined as in FIGS. 1, 2, 4 and 5. The mechanism of image recording and negative development are essentially alike that described above, but the transport mechanism is sufficiently unique to warrant its own description.

After imaging and introduction of the processing solution development proceeds as described in FIG. 3a, leaving an imagewise distribution of immobile azomethine and indoaniline dyes and unreacted 4-equivalent color formers (corresponding to unexposed portions of the film package). After development has proceeded substantially to completion a timing layer which contains the diazonium salt or diazonium precursor breaks down or solubilizes thus releasing the entrapped species. The mobile diffusion actuating diazonium now migrates throughout the film package coupling with the remaining 4-equivalent color formers to produce an imagewise diffusion of azo dyes (see FIG. 3d). The azo dyes are in turn transferred to the receiving portions of the package where oxidized developer, generated by incorporated oxidizing agent converts them into azomethine or indoaniline dyes. To facilitate understanding of the preferred embodiments in the examples, only diazonium salts "(2)" and "(5)" are illustrated below, but all salts disclosed can be used, and it should be understood that these salts are only a few of many salts or of aromatic azo sulfones or of diazonium precursors which provide the new and superior results of the invention.

EXAMPLE 1

To 50 ml of a bromiodide emulsion containing 5 percent of silver was added 0.6 g of diazonium salt "2" and 3 ml of a color former dispersion containing 8 percent color former as shown in FIG. 3a in 12 percent of dispersing oils dibutylphthalate and tricresylphosphate. The resulting formulation was coated with the aid of surfactants such as Saponin or Tergitol No. 4, on a clear film base of cellulose acetate butyrate. The dried coating, containing about 1 g of silver/ m^2 , was exposed imagewise and brought into contact with an opaque receiving sheet containing 1-(4-decoxyphenyl)-biguanide in gelatin as a mordant with a concurrent application of a processing solution of the following formulation:

Benzyl alcohol	2.0 ml
Nitrilotriacetic acid, disodium salt	4.0 g
Alipal CO-436	0.83 ml
Na_2SO_3	4.0 g
CD-2	5.0 g
KOH	21.0 g
Boric Acid	18.0 g
NaCl	2.5 g
Hydroxylamine Sulfate	2.0 g
Metol	0.10 g
Phenidone B	0.10 g
2% Carboxymethyl Cellulose	500.0 cc
H_2O to	1.0 ltr
pH = 10.7	

CD-2 is a color developer which is 4-N,N diethyl amino 2 methyl aniline monohydrochloride or salt as supplied by Eastman Kodak Co.

Tergitol is defined in Hackh's Chemical Dictionary, 3rd Edition, at page 836 as a polyethylene oxide surfactant.

Alipal CO-436 is ammonium salt of sulfated nonyl phenoxy poly(ethylene oxy) ethanol.

After 20 seconds of contact, the receiving sheet was peeled from the negative. At this point, the negative material exhibited a cyan image on an orange-yellow background and the mordant-receiving sheet exhibited a positive orange-yellow image. Treating the receiving sheet with 5 percent potassium ferricyanide solution, followed by washing, resulted in a positive cyan image.

EXAMPLE 2

A negative layer similar to that of Example 1 but without the incorporation of the diazonium salt was coated and processed as in Example 1. After five minutes, the negative and receiving sheet were separated. The receiving sheet was treated with 5 percent potassium ferricyanide but no color was generated, thus indicating that all diffusion of color providing species in Example 1 was induced by azo formation.

EXAMPLE 3

A mordant bearing receiving sheet was prepared by coating a subbed white opaque film base such as baryta coated paper, with a gelatin solution of 1-(4-decoxyphenyl)biguanide. The coating formulation was prepared by adding to 500 ml of a 3 percent gelatin solution, 3.0 g of 1'-(4-decoxyphenyl)biguanide and 1.5 ml of glacial acetic acid. The mixture was held at 50°C until solution was complete (about 15 minutes) and then cooled to 40°C with 2.5 ml of a 6 percent acetone solution of 1,4-butanediol diglycidyl ether added as a hardener. The resulting gelatin solution was then dip coated at 40°C to a thickness which would generate a concentration equivalent to that of the azo dye to be mordanted.

EXAMPLE 4

On a clear cellulose acetate butyrate film base was coated, as a mordant, an acid treated gelatin solution to a thickness of 10 μ . Over this receiving layer was then coated a 4 percent lime treated gelatin solution exhibiting an isoelectric point at pH 5 containing titanium dioxide at a concentration of 10 percent. The thickness of this second layer was 8.7 μ and it thus gave transmission readings of 1.0 for blue, green, and red light and reflection readings of 0.1 or less.

EXAMPLE 5

A layer of gelatin bearing diazonium salt was prepared by dissolving 2.0 g of diazonium salt "5" in 100 ml of 6 percent gelatin solution and adding 10 ml of 10 percent acetic acid, 5 ml of 8 percent Saponin and 2 ml of 5 percent triacrylformal. The solution was then coated to 10 μ thickness on clear cellulose acetate butyrate film base.

EXAMPLE 6

A 2 percent ethyl cellulose phthalate (ECP) solution was made by dissolving 20 g of ECP in 150 cc of methanol and 2.0 cc of concentrated NH₄OH. The mixture was heated on a steam bath until solution was complete. To this clear solution was very slowly added 850 cc of water at 5°-10°C. The resulting formulation was then kept at icebath temperatures to release trapped air bubbles. The pH was now at the preferred pH of 7.0 to 7.2.

EXAMPLE 7

To 1.0 ltr. of 2 percent ECP solution prepared in Example 6 was added 2.2 ltr. of water and 0.4 ltr. of polyurethane latex (40 percent). This solution was then coated at 5 and 10 μ thicknesses over the diazonium coating of Example 5. A table of time versus timing layer thickness for various pH ranges is recorded below. The testing scheme utilized a water soluble diazonium coupler at a concentration of 0.1 g per 100 ml of alkaline solution. Potassium hydroxide at various concentrations was employed to adjust the pH levels.

Thickness of ECP	Time (Sec.)					
	pH 13.3	pH 13.0	pH 12.8	pH 12.5	pH 12.2	pH 11.8
0	1	3	4	4	7	16
5 μ	5	7	14	14	33	90
10 μ	7	10	14	22	67	180

EXAMPLE 8

National Starch Resin 1310 (1:4 crotonic acid, vinyl acetate co-polymer) was found to be a viable timing species when solvent coated at a concentration of 10g solid in a 200 ml ethanol/methanol mixture (1:1). To determine its delaying action the resin was coated over a color paper stock and processed in the developer formulation of Example 1 in white light. Using untreated stock as a standard the National Starch resin was found to give a 15 second delay at 5 μ thickness and a 30 second delay at 10 μ thickness at a pH of 10.7.

EXAMPLE 9

Gantrez ES 425 (the half butyl ester of maleic anhydride methyl vinyl ether copolymer) made by GAF Corporation, was found to give a delay to the penetration of alkali. The Gantrez was dip coated to a layer thickness of 1.5 μ onto white lighted panchromatic film from a 4 percent solution in absolute alcohol. A 1 percent hydroquinone solution at pH 11.5 with sodium hydroxide as the alkali indicated a timing delay of 0.8 minutes at 75°F.

EXAMPLE 10

Over the receiving layers as described in Example 4

was coated a cyan dispersion (no silver) as described in Example 2. This package was then soaked in an ammonium hydroxide solution, pH 12.3, for one minute and placed in contact with a portion of the diazonium coating mentioned in Example 5 and imaged with UV radiation. After a contact of 30 seconds an azo dye image was observed in the positive portion of the package (behind the TiO₂ layer). The pressure sheet was peeled off and the positive was soaked in the developer formulation of Example 1 and converted to the cyan indoaniline dye by soaking for 15 seconds in 2 percent ammonium persulfate solution.

EXAMPLE 11

A sample of the diazonium releasing package described in Example 7 with a thickness of ECP of 5 μ was overcoated with the negative formulation of Example 2 to a thickness of 3.0 μ . The negative was imaged through a photographic stepwedge and then placed in contact with a receiving sheet of a construction and formulation of Example 3 which had a thickness of 5 μ with a simultaneous application of the processing solution mentioned in Example 1 but adjusted to pH 12.0 with KOH. After a contact time of 45 seconds, an orange positive image (azo dye) on a yellow background (diazonium salt) was observed. Treating the receiving sheet with 2 percent ammonium persulfate discharged the yellow diazonium and converted the orange azo dye to the cyan indoaniline dye.

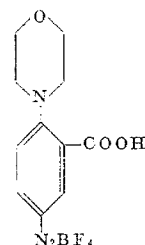
EXAMPLE 12

A negative package is coated as in Example 11 but with one addition. Over the cyan containing emulsion is coated, to a thickness of 5 μ , a dispersion of oil soluble long chain 4equivalent coupler or a solution of long chain hydrophilic coupler in gelatin. The film package is exposed and processed as in Example 11. After a contact time of 45 seconds, an orange positive image on a white background is observed. The yellow diazonium salt corresponding to developed areas does not proceed to the receiving sheet due to coupling in this barrier layer of 4-equivalent coupler. Generation of the cyan image is as in Example 11.

EXAMPLE 13

SYNTHESIS OF NOVEL DIAZONIUM SALTS

a. 3-Carboxy-4-morpholinobenzenediazonium fluoborate

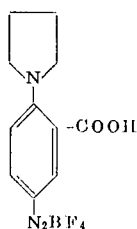


20.1 grams 2-chloro-5-nitrobenzoic acid was added in portions to 87 ml morpholine. The temperature of the thick mixture rose to 70°C after being stirred at reflux temperature for 5 hours, the mixture was poured into ice water, made acidic with conc. HCl, filtered, dried and recrystallized from ethanol to give 20.3 g 2-morpholino-5-nitrobenzoic acid, melting point 168° - 170°C. This nitro compound was reduced catalytically to give 5-amino-2-morpholinobenzoic acid, melt-

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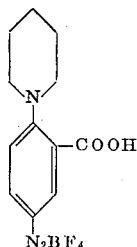
ing point 307–8°C. The amine was then diazotized in ethanol to give 3-carboxy-4-morpholinobenzenediazonium fluoborate, dec. 146°C.

b. 3-Carboxy-4-(1-pyrrolidinyl)benzenediazonium fluoborate



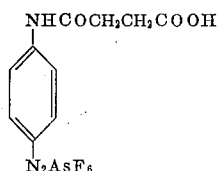
2-Chloro-5-nitrobenzoic acid was reacted with pyrrolidine and gave 5-nitro-2-(1-pyrrolidinyl)benzoic acid, melting point 224–6°C. The nitro was reduced to give the amine, melting point 205–8°C, which was diazotized in dilute HCl and gave 3-carboxy-4-(1-pyrrolidinyl)benzenediazonium fluoborate, dec. 157–8°C.

c. 3-Carboxy-4-piperidinobenzenediazonium fluoborate

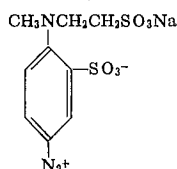


5-Nitro-2-piperidinobenzoic acid, prepared according to *Journal Chemical Society* 1117 (1927), was reduced catalytically and the amine, melting point 232–5°C, was diazotized in ethanol to give the diazo, dec. 140–1°C.

d. 4(3-carboxypropionamido)benzenediazoniumhexafluoroarsenate



p-Nitrosuccinamic acid, prepared as described in *Journal American Chemical Society*, 67, 1220, was reduced catalytically and the amine, melting point 180–1° dec., was diazotized in dilute HCl at room temperature. The diazo was isolated as the hexafluoroarsenate by the addition of a 3.5 molar solution of hexafluoroarsenic acid. The product decomposed at 127–8°C.

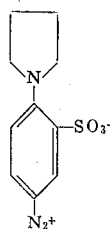


Sodium 2[methyl(2-sulfoethyl)amino]-5-nitrobenzenesulfonate was prepared following a method described in Part II of Bios Report No. 986 and reduced

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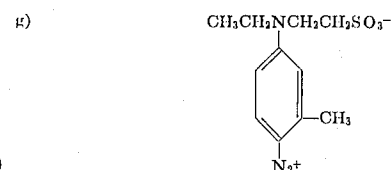
catalytically in ethanol-water (2:1) to give the amine which was diazotized in dil. HCl, giving the desired sodium 4-[-methyl(2-sulfoethyl)amino]-3-sulfobenzenediazonium inner salt. Dec. 239–241°C.

f. 4(1-pyrrolidinyl)3-sulfobenzenediazonium inner salt



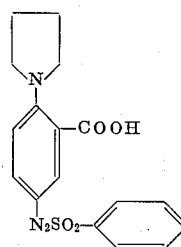
2-Pyrrolidinyl-5-nitrobenzenesulfonic acid was prepared by adding 72.4 g of 2-chloro-5-nitrobenzenesulfonic acid in portions to 134 ml pyrrolidine keeping the temperature below 65°C. After the addition the reaction was allowed to stir at reflux temperature for 7 hours and poured into 800 ml ice water. The solution was made strongly acidic with conc. HCl until precipitation of yellow crystals was complete. Filtered and washed with a little dil. HCl, the moist cake was recrystallized from water to give 70.7 g of the nitro compound dec. 178–9°C.

The above nitro was reduced catalytically to give the amine, dec. 255–56°C. 24.2 g of the amine was diazotized in dil. HCl and isolated by pouring the diazo solution into ethanol. After cooling the diazo was filtered, washed with ethanol and vacuum dried to give 19.3 g of diazo, sudden dec. at 157°C.



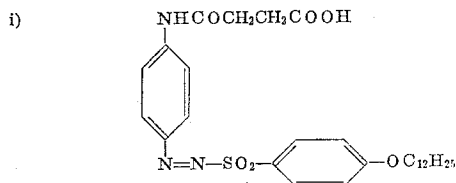
4-Amino-N-ethyl-3-methyl-N-(β-sulfoethyl)aniline was prepared according to the procedure described in *Journal American Chemical Society*, 78, 5827. This amine (14.0 g) was diazotized in ethanol with n-butyl nitrite to give the desired diazo (12.0 g) 4-[-methyl(2-sulfoethyl)amino]o-toluene-diazonium inner salt. Darkens and dec. <200°C.

h. 5-Phenylsulfonylazo-2(1-pyrrolidinyl)benzoic acid



5-Nitro-2-pyrrolidinylbenzoic acid (15 g) was dissolved in 100 ml water, 37 ml formic acid and 11 ml conc. HCl. This solution was diazotized at 5°–10°C with 11.6 ml sodium nitrite (5M). After one-half hour the excess nitrite was destroyed with sulfamic acid and 13.1 g sodium benzenesulfinate dissolved in 30 ml water was added. The mixture was allowed to stir for

1 hour and the gummy precipitate started to crystallize on standing overnight under refrigeration. The solid was filtered and triturated with methanol, filtered, vacuum dried to give 11.4 g of diazo sulfone dec. 127–130°C.



4-Dodecyloxybenzenesulfonyl chloride (10 g), prepared according to *Journal Chemical Society* (1946) 865, 25 ml ether, 1 ml water was treated with 5 g zinc dust and allowed to stir at room temperature for one-half hour. Added an additional 50 ml ether and the mixture was stirred at reflux temperature for 3 hours. The mixture was filtered and the filter cake was treated with a solution of 5 g sodium carbonate dissolved in 250 ml. water. The mixture was heated to the boil and the insolubles were hot filtered off. The filtrate cooled to give 5.9 g of sodium 4-dodecyloxybenzenesulfinate.

2 g of the above sulfinate was dissolved in a mixture of 80 ml of water, 80 ml ethanol, 80 ml methanol. To this filtered solution was added a solution of 2 g 4-(3-carboxypropionamido)-benzenediazonium hexafluoroarsenate in 40 ml water and 5 ml ethanol. The yellow precipitate was stirred at room temperature for 15 minutes. The precipitate was filtered, washed with water and dried in a vacuum to give 2.8 g of N-[p-(p-Dodecyloxyphenyl-sulfonylazo)phenyl]succinamic acid dec. 111–113°C.

We claim:

1. A photographic film package for producing a positive color image, comprising:

- a. at least one light sensitive silver halide emulsion layer, each emulsion layer being sensitized to the spectrum of a different primary color;
- b. each said emulsion layer containing a 4-equivalent color former which yields a complementary color to the primary color of said emulsion layer, said color former being incorporated in a high boiling photographically inert oil droplet dispersion uniformly distributed within said emulsion layer; said color former having substantially no water solubility and substantially no mobility at pH below about 9 and being capable of reacting with oxidized color developer to form an immobilized coupled product at exposed areas;
- c. a benzene diazonium salt, or precursor thereof, containing at least one group independently selected from carboxy and sulfo and being capable of azo coupling with said color former to form a highly diffusible azo dye;
- d. one of said color former and said diazonium salt or precursor thereof being non-diffusible at the development pH and the other being at least slightly diffusible at the development pH to allow said azo coupling to proceed, after imagewise exposure and color development of said package with an alkaline processing solution containing a color developer, between color former that has not reacted with oxidized color developer and said diazonium com-

pound or precursor thereof to form said azo dye; and

e. a receiving portion having chemical means for mordanting azo dye that has diffused thereto and converting mordanted azo dye into immobilized azomethine or indoaniline dyes.

2. The package according to claim 1, wherein the color former is non-diffusing at the development pH and the benzene diazonium salt or precursor thereof is highly diffusible at the development pH, the benzene diazonium salt or precursor thereof being separated from said color former by a timing layer that releases said diazonium salt or precursor thereof for diffusion after color development is substantially completed.

3. The package according to claim 1, wherein c) is a benzene diazonium salt or precursor thereof which is non-diffusing at the development pH and which is incorporated in a separation layer adjacent each said emulsion layer, and said color former is slightly diffusible at the development pH to at least an extent to enable diffusion of the color former from its emulsion layer to the benzene diazonium precursor-containing layer adjacent thereto.

4. The package according to claim 1, wherein said color former and said benzene diazonium salt or precursor thereof are both in the emulsion layer.

5. The package according to claim 1, wherein the benzene diazonium precursor is a benzene azo sulfone.

6. The package according to claim 2, wherein the color former is essentially non-diffusible at pH less than 11.5 and the benzene diazonium salt or precursor thereof is 3-carboxy-4-(1-pyrrolidinyl)benzenediazonium fluoborate, 5-phenylsulfonylazo-2-(1-pyrrolidinyl) benzoic acid, or 4-[methyl-(2-sulfoethyl)-amino]-3-sulfobenzenediazonium inner salt.

7. The package according to claim 3, wherein the non-diffusing benzene diazonium precursor is N-[p-(dodecyloxy-phenylsulfonylazo)-phenyl] succinamic acid.

8. The package according to claim 4, wherein the benzene diazonium salt is 3-carboxy-4-(1-pyrrolidinyl)-benzene-diazonium fluoborate.

9. The package according to claim 1 wherein the polymeric timing layer is the half butyl ester of maleic anhydride methyl vinyl ether copolymer.

10. The package according to claim 1 wherein the polymeric timing layer is 1:4 crotonic acid, vinyl acetate copolymer.

11. The package according to claim 1 wherein the polymeric timing layer is a mixture of ethyl cellulose phthalate and polyurethane latex.

12. A photographic film package for producing a positive color image, comprising:

- a. at least one light sensitive silver halide emulsion layer, each emulsion layer being sensitized to the spectrum of a different primary color;
- b. each said emulsion layer containing a 4-equivalent color former which yields a complementary color to the primary color of said emulsion layer, said color former being incorporated in a high boiling photographically inert oil droplet dispersion uniformly distributed within said emulsion layer; said color former having substantially no water solubility and substantially no mobility at pH below about 9 and being capable of reacting with oxidized color

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developer to form an immobilized coupled product at exposed areas;

- c. said emulsion layer also containing a benzene diazonium salt, or precursor thereof, containing at least one group independently selected from carboxy and sulfo and being capable of azo coupling with said color former to form a highly diffusible azo dye after imagewise exposure and color development of said package with an alkaline processing

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- solution containing a color developer; and
d. a receiving portion having chemical means for mordanting azo dye that has diffused thereto and converting mordanted azo dye into immobilized azomethine or indoaniline dyes.

13. The package according to claim 12, wherein the benzene diazonium salt is 3-carboxy-4(1-pyrrolidinyl)-benzenediazonium fluoborate.

* * * * *