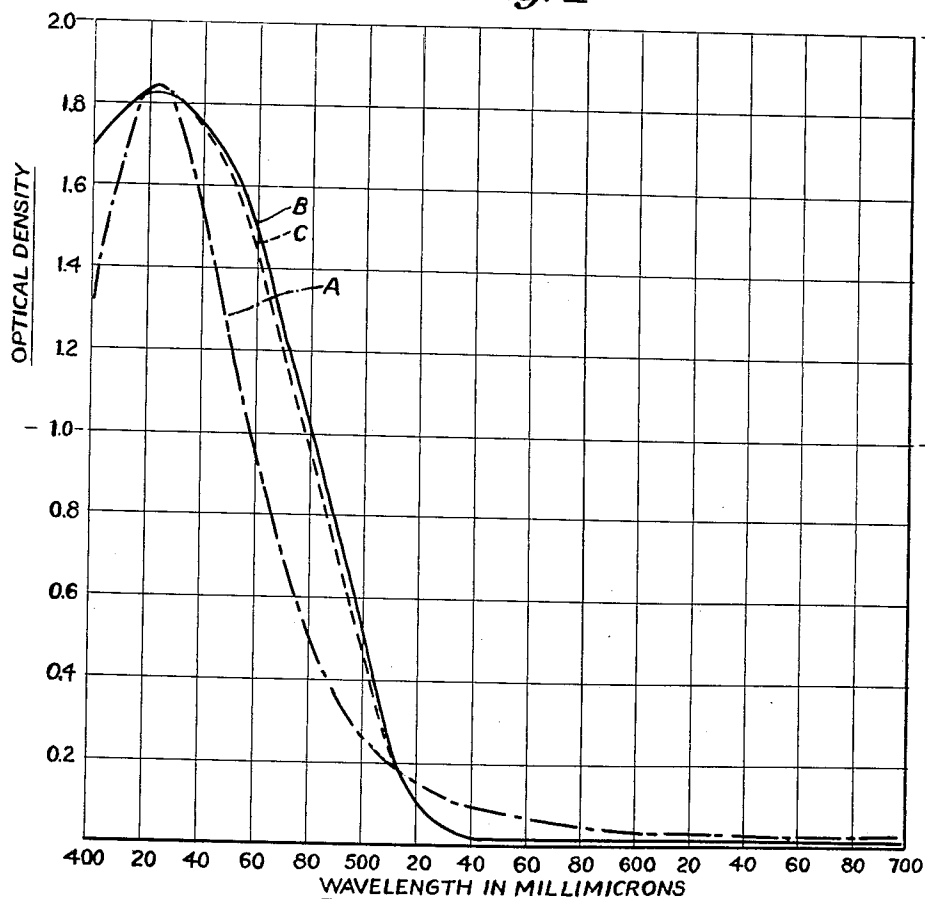


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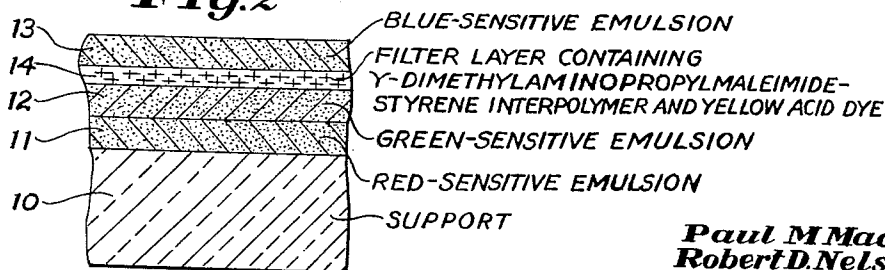
P. M. MADER ETAL  
YELLOW FILTER LAYERS FOR MULTI-LAYER  
PHOTOGRAPHIC COLOR ELEMENTS  
Filed Nov. 25, 1957

3,016,306

**Fig. 1**



**Fig. 2**



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3,016,306

## YELLOW FILTER LAYERS FOR MULTI-LAYER PHOTOGRAPHIC COLOR ELEMENTS

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4 Claims. (Cl. 117—33.3)

This invention relates to a process for preparing yellow filter layers for photographic multi-layer color elements, and to new photographic multi-layer color elements thereby obtained.

In color photography, it is customary to employ in subtractive processes a multi-layer element comprising a support having coated thereon a plurality of light-sensitive layers which have been sensitized to particular regions of the spectrum. For example, it is customary to employ a photographic element comprising a transparent, flexible support having coated thereon three light-sensitive photographic emulsion layers, one of these being sensitive to the red, one to the green and the third to blue. While the photographic element might contain additional layers, such as gelatin interlayers, the photographic element always contains at least two light-sensitive emulsion layers in the processes contemplated by the present invention.

A typical photographic element useful in our invention comprises a support having a red-sensitive emulsion coated thereon, a green-sensitive emulsion coated on top of the red-sensitive emulsion, a filter layer for absorbing blue light coated on top of the green-sensitive layer, and a blue-sensitive emulsion layer coated on top of the filter layer. It is immediately apparent that other arrangements for subtractive color reproduction are possible, such as a reversal of the order of the green- and red-sensitive emulsions, or the use of a single emulsion coating containing discrete areas responsive to red light and other discrete areas responsive to green light. The latter emulsions are frequently referred to in the art as mixed packet emulsions. Since the red- and green-sensitive emulsions are also responsive to blue light, it is apparent that the yellow filter layer is an integral part of the photographic elements contemplated by the instant invention, inasmuch as this layer absorbs substantially all of the blue light which is transmitted by the blue-sensitive emulsion layer.

It is well known that colloidal silver can be used as the light-absorbing ingredient in the yellow filter layers. However, it is recognized that colloidal silver has certain serious drawbacks to its use in these filter layers. For example, colloidal silver has a ratio of green to blue density higher than desirable, and, in addition, the minute particles of colloidal silver (i.e., Carey-Lea silver) can act as centers for physical development, which may have an undesirable effect on the saturation and color balance of the resulting reproduction. It has been proposed in a number of technical articles and patents to replace the colloidal silver with various organic dyes. This alternative thus avoids certain of the undesirable effects of the colloidal silver, such as the physical development factor mentioned above, but other new difficulties are introduced at the same time. For example, it is difficult to find dyes having the proper absorption characteristics, i.e., high density to blue light but little or no density to green and red light, and at the same time remain in the layer in which they are incorporated. That is, the dyes are likely to migrate from the filter layer into the blue-sensitive emulsion layer, where their presence might have serious effects. To overcome the migration problem, it has been suggested that the dye be fixed in the filter layer by means of a mordant, which may be a high molecular weight polymer having an ionic charge opposite to that of the light-

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absorbing dye. For example, the light-absorbing yellow dye might be an acid dye, in which case the organic mordant would be a cationic material. In the preparation of mordanted filter layers, it is generally the practice to simply mix an aqueous solution containing the desired filter dye with the organic mordant, which might also contain a colloid, such as gelatin, albumen, etc., and coat the mixture onto an emulsion layer or an interlayer. This method has the disadvantage in many instances of causing a precipitate of the mordant and dye to form. The precipitate then causes diffusion of the light transmitted by the blue-sensitive layer, so that proper color balance is not rendered.

The process of our invention is concerned with organic mordants and yellow filter dyes and a means of preventing the formation of large precipitates or aggregates which might have a serious effect upon the proper rendition of the colors in the originals being reproduced.

It is, therefore, an object of our invention to provide an improved process for preparing yellow filter layers of multi-layer photographic color elements. Another object is to provide novel multi-layer photographic elements for color photography. Other objects will become apparent from a consideration of the following description and examples.

According to our invention, we avoid the aforementioned difficulties accompanying the use of mordant-filter dye combinations by incorporating the filter dye in a layer contiguous to the layer containing the mordant. The filter dye then migrates spontaneously from the layer in which it has been incorporated into the layer containing the mordant. The dyes used in our invention are soluble in water or dilute alkaline solutions and they have their maximum absorption between 400 and 500 millimicrons. Moreover, the filter dyes used in our invention have very slight absorption in the green and red regions of the spectrum. The layer in which the filter dyes are incorporated can be conventional interlayers, such as gelatin, polyvinyl alcohol, etc., interlayers, or these layers can be photographic emulsions which have been sensitized to a given spectral region. The layer in which the filter dye is initially incorporated contains no material, such as a mordant, which would prevent migration of the dye to the layer containing the mordant. Generally, the mordant is incorporated into a layer containing a hydrophilic colloid, such as gelatin, albumen, agar agar, etc.

The yellow filter dyes useful in practicing our invention are generally acid dyes. The dyes contain one or more carboxylic acid or sulfonic acid groups, or a water-soluble salt of such groups (e.g., sodium, potassium, etc.).

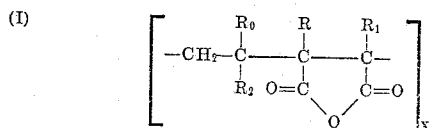
The mordants useful in practicing our invention are basic in character and have a molecular weight of at least 250. These mordants are readily dispersible in water, or water containing an ionic dispersing agent. Particularly useful mordants comprise those having molecular weight of at least 250, at least one tertiary or quaternary nitrogen atom, and sufficient hydrophilic properties to enable these mordants to be dispersed readily in water. The most useful mordants in our invention comprise those derived from a linear polymer or interpolymer. Representative of such polymers are mordants obtained from a monoethylenically-unsaturated, polymerizable compound containing a dialkylamino group, or polymerized, monoethylenically-unsaturated compounds which have been modified to contain a dialkylamino group.

Typical mordants which can be used in our invention are piperidyl cellulose, chloromethylated polystyrene which has been solubilized by treatment with pyridine (see U.S. Patent 2,694,702), dialkylaminoalkyl esters or dialkylaminoalkylamino amides (e.g., such as those described in Carroll et al. U.S. Patent 2,675,316, issued April 13, 1954), reaction products of carbonyl contain-

ing polymers and aminoguanidine or their salts (e.g., those derived by reacting polyvinyl alkyl ketones or aldehydes, such as polyacrolein, polyvinyl methyl ketone, etc., with aminoguanidine, as described in the copending application of L. M. Minsk, Serial No. 554,111, filed December 19, 1955, now U.S. 2,882,156, granted April 14, 1959), polymers obtained by reacting a dialkylaminoalkyl amine with a polymer of maleic anhydride or a derivative of maleic anhydride (e.g., as described in the copending application of L. M. Minsk and H. L. Cohen, Serial No. 663,810, filed June 5, 1957), etc. Other mordants which can be used in our novel process comprise those described in Fowler et al., U.S. Patent 2,721,852, issued October 25, 1955, and Fowler et al. U.S. Patent 2,798,063, issued July 2, 1957. Non-polymeric high molecular weight mordants which can be used in our invention comprise long-chain alkyl quaternary ammonium compounds, such as decamethylene-bis-trimethylammonium bromide, n-octyl tri- $\beta$ -hydroxyethylammonium chloride, n-dodecyl diethyl- $\beta$ -hydroxyethylammonium chloride, etc. (e.g., tetraalkylammonium halides containing an alkyl group having at least 8 carbon atoms).

Particularly useful mordants in our invention comprise those derived from maleic anhydride, or a derivative thereof as mentioned above. These mordants have been found to be particularly free of precipitation defects and can frequently be used in combination with acid yellow filter dyes by simply mixing the mordant with the filter dye.

Particularly useful interpolymers of maleic anhydride, or its substituted derivatives, include those polymers represented by the following general formula:



wherein R, R<sub>0</sub> and R<sub>1</sub> each represents a hydrogen atom or a lower alkyl group, such as methyl, ethyl, etc., R<sub>2</sub> represents a hydrogen atom, an alkyl group (e.g., methyl, ethyl, etc.), a monocyclic aryl group (e.g., phenyl, tolyl, etc.) or a carbalkoxyl group (e.g., carbomethoxyl, carbethoxyl, etc.) and x represents a large whole number, such as a whole number greater than about 10. Maleic anhydride interpolymers included by Formula I above have been previously described in numerous prior art references. Such interpolymers are generally derived from monomers, such as ethylene, styrene, isobutylene, acrylic esters, etc. Instead of using maleic anhydride itself in the preparation of these interpolymers, it is possible to use maleic or fumaric acid esters to equal advantage, although the reaction times are generally lengthened in those cases where the ester derivatives are used in place of the anhydride. In like manner, the interpolymers can be obtained from maleic acid or fumaric acid.

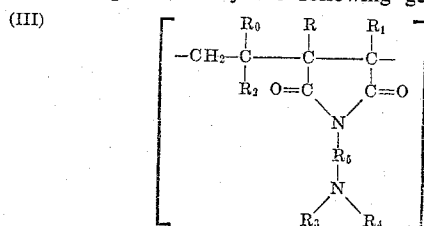
Interpolymers of the type represented by Formula I above (including the compounds of Formula I or the derivatives illustrated above) are reacted with disubstituted diamines of the type represented by the following general formula:



wherein R<sub>3</sub> and R<sub>4</sub> each represents a lower alkyl group (e.g., methyl, ethyl, n-propyl, n-butyl, etc.) or R<sub>3</sub> and R<sub>4</sub> together represent the atoms necessary to complete a piperidine or morpholine ring, and R<sub>5</sub> represents an alkylene group (e.g., ethylene, propylene, butylene, pentylene, etc., especially an alkylene group containing 2 to 3 carbon atoms).

The reaction of the interpolymers of Formula I with the diamines of Formula II need not be on an equimolar

basis, although generally it is advisable to use sufficient diamine to insure reaction of substantially all (i.e., 100%), but at least about 75% to 80%, of the anhydride units in the interpolymers. Where the interpolymers used contains acid groups or ester groups in place of the anhydride units illustrated in Formula I, it is generally preferable to use sufficient amine to react with all of these free acid groups or ester groups. As indicated above, the first step in the reaction of the compounds of Formula I with those of Formula II leads to the formation of derived polymers containing carboxylic amide groups as a result of the reaction of the primary amino group of the compounds of Formula II with the anhydride groups of the polymers represented by Formula I. Further heating either alone or in the presence of a dehydrating agent, such as acetic anhydride, propionic anhydride, etc., leads to the formation of the mordants of our invention which can be represented by the following general formula:

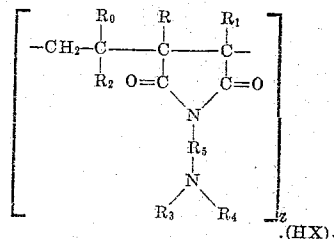


wherein R, R<sub>0</sub>, R<sub>1</sub>, R<sub>2</sub>, R<sub>3</sub>, R<sub>4</sub> and R<sub>5</sub> each have the values given above and z represents a large whole number, such as a whole number greater than about 10 (z may be the same as x, depending upon the molar quantity of the diamine used, which is used in an amount as indicated above to react with from about 75% to 80% of the anhydride units, as a minimum).

Under the above preparative conditions the product will contain combined acid. This acid may be removed by treatment with a base. All, or a portion of all, of the residual anhydride units are hydrolyzed to carboxylic acid units under the above conditions.

The preparation of the mordants used in our invention can be carried out in the presence of an inert diluent, such as dioxane, benzene, acetone, etc. The first step of the reaction resulting in the formation of carboxylic amide units in the interpolymers is generally carried out at about the temperature of the steam bath. After the addition of the dehydrating agent, the heating is continued for a period of time sufficient to cause reaction of most of the anhydride, acid or ester groups present in the interpolymers. The preparation of imides has been previously illustrated in U.S. Patent 2,313,565. The imides of Patent 2,313,565 generally contain ether groups attached to the linear polymer chain, and we have found that such groups generally cause color formation in the resulting imide polymers. In our process, such ether groups and undesirable free acid groups are avoided.

While the mordants of our invention as illustrated in Formula III above are in the form of their free bases, these mordants are customarily used in aqueous acid solutions so that at least a portion of the polymer units are in the following form:



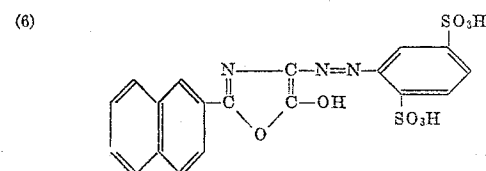
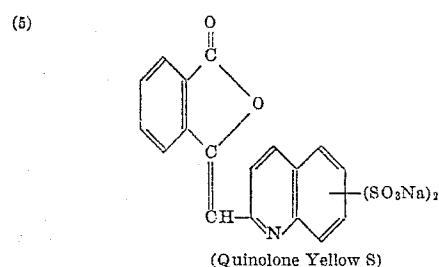
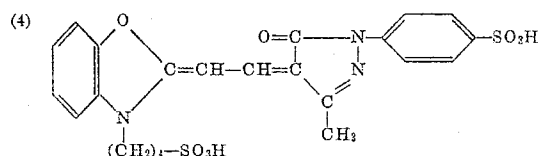
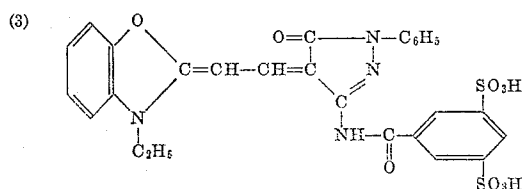
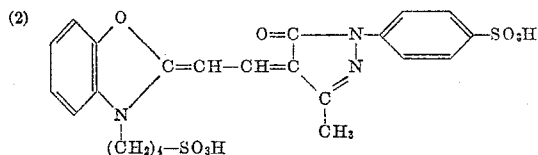
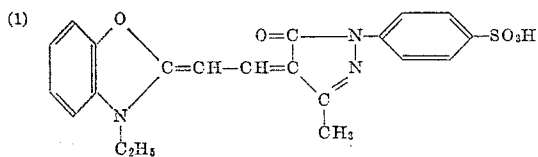
wherein R, R<sub>0</sub>, R<sub>1</sub>, R<sub>2</sub>, R<sub>3</sub>, R<sub>4</sub>, R<sub>5</sub> and z each have the values given above, X represents an acid radical (inorganic or organic), such as lactyloxy, glycolyloxy, acetoxy, propionyloxy, alkanesulfonyloxy (e.g., methanesulfonyloxy,

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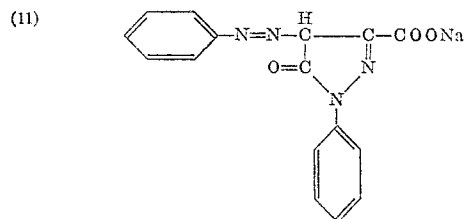
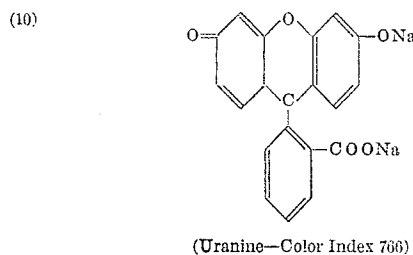
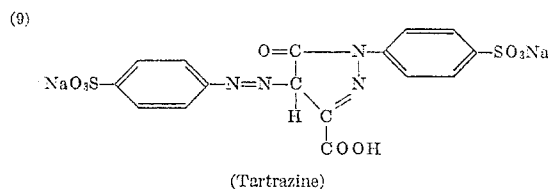
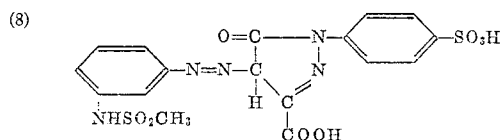
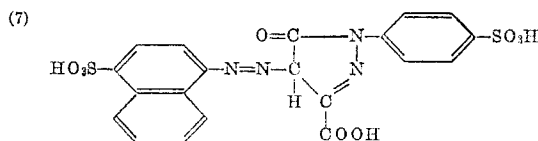
ethanesulfonyl, n-butesulfonyl, etc., especially such radicals containing from 1 to 4 carbon atoms), chloride, etc. and  $y$  represents at least  $\frac{1}{2}z$  but not more than  $z$ . Of course, when a carboxylic anhydride is used as the dehydrating agent as shown above, some of the free acid formed forms an acid-addition salt with the polymeric imide. In those cases where the free base or imide is obtained as such, sufficient acid (in aqueous form) can be added until the aqueous solution is rendered acid. The amount of acid needed for this purpose will vary, depending on the particular acid and the intended use of the mordant. In general, sufficient acid is present or used to give a pH below about 6.0.

While maleic anhydride generally enters polymerizations in a 1:1 ratio with a comonomer, sometimes it interpolymerizes in smaller ratios, such as 1:2 (i.e., 33% maleic anhydride units). Maleic anhydride derivatives, such as maleic or itaconic esters, frequently interpolymerize at various ratios (U.S. Patent 2,298,039). The useful interpolymers of Formula I above can contain between about 33 and 50 mol. percent maleic anhydride (or derivative) units. Especially useful interpolymers are those containing a molar ratio of 1:1 of maleic anhydride units.

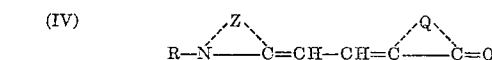
Particularly useful yellow dyes for the process of our invention comprise the following:



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Dyes 1, 2, 3 and 4 above are merocarbocyanine dyes. These dyes belong to a particularly useful group of dyes for our invention which can advantageously be represented by the following general formula:



wherein R represents an alkyl group such as methyl, ethyl, n-propyl, n-butyl, isobutyl,  $\beta$ -sulfoethyl, 3-sulfo-butyl, 4-sulfobutyl, etc., Z represents the non-metallic atoms necessary to complete a heterocyclic nucleus of the benzoxazole series (including benzoxazole and benzoxazole substituted by simple substituents, such as methyl, ethyl, phenyl, methoxyl, ethoxyl, chlorine, bromine, etc.), and Q represents the non-metallic atoms necessary to complete a heterocyclic nucleus of the pyrazolinone series, provided that the nucleus defined by Q contains at least one acid substituent or radical in those cases where R represents a hydrocarbon group. The most useful dyes of Formula IV comprise those dyes containing at least two hydrocarbon radicals or groups which have been further substituted by a carboxyl or sulfo group. The yellow filter dyes of our invention are spontaneously removed during conventional color processing or they can be easily removed at any time simply by treatment with an aqueous alkaline solution. Certain of these dyes may actually be decolorized or bleached during processing, thus making complete removal thereof unnecessary, particularly in a negative process.

The following examples illustrate the manner of incorporating the yellow filter dyes of our invention in a hydrophilic colloid layer containing a mordant:

## EXAMPLE 1

5.5 g. of a 12% aqueous dispersion of a mordant obtained by condensing polyvinyl methyl ketone with aminoguanidine, as described in Minsk application Serial No. 554,111, now U.S. 2,882,156, granted April 14, 1959, mentioned above, were added to 5.0 cc. of a 10% aqueous gelatin solution (pH=6.5). To this mixture was added a dispersion of 0.07 g. of a polyethylene glycol oleyl ether (Atlas G 3920—spreading agent) suspended in 29.5 ccs. of water. After intimately mixing these ingredients, the resulting dispersion was coated on an ordinary cellulose acetate film support at a wet thickness of .003."

0.5 g. of 3-benzoylacetamino-4-methoxy- $\omega$ (2',4'-ditertiaryamylphenoxy)acetanilide prepared as described in the copending application of F. C. McCrossen, P. W. Vittum and A. Weissberger, Serial No. 575,099, filed March 30, 1956 (now U.S. 2,875,057, granted February 24, 1959), was dissolved in a mixture of 1.0 cc. of di-n-butylphthalate and 2.0 cc. of ethyl acetate by heating with stirring. The resulting solution was mixed with 22.0 ccs. of a 10% aqueous gelatin solution containing 2.0 ccs. of 5% Alkanol B (a sodium triisopropyl naphthalene-sulfonate). The resulting mixture was put through a colloid mill four times to effect dispersion. A dispersion of 0.30 g. of tartrazine in 17.0 ccs. of water containing .07 g. of a polyethylene glycol oleyl ether (Atlas G 3920) was prepared. The gelatin dispersion containing the acetanilide coupler and the dispersion containing the tartrazine were then added to 7.7 ccs. of an ordinary unsensitized gelatino-silver-bromide emulsion and the ingredients thoroughly mixed. The resulting dispersion was then coated over the layer containing the mordant to a wet thickness of .006". The coatings were then dried in the usual manner and cut into sections. Inspection of the sections under the microscope established that the tartrazine dye had completely diffused from the silver bromide layer into the mordant layer, leaving no visible trace of dye in the top layer containing the color coupler.

## EXAMPLE 2

This example was prepared in exactly the manner shown in Example 1, except that 2.5 g. of the mordant in 3 ccs. of water were employed in place of the 5.5 g. of mordant used in Example 1, and 0.20 g. of dye 11 above were used in place of the tartrazine. As in the case of the coatings of Example 1, the dye completely diffused from the silver halide emulsion layer into the layer containing the mordant.

Instead of incorporating the yellow acid dye in the topmost silver halide emulsion layer as shown in Examples 1 and 2, the filter dye can be incorporated in the lower silver halide emulsion layer, such as the red-sensitive or green-sensitive silver halide emulsion layer with which it is in contact. The blue-sensitive silver halide emulsion layer is then coated over the filter layer in the customary manner. The unsensitized silver halide emulsion layers employed in Examples 1 and 2 were blue-sensitive and had little or no green and red sensitivity. The particular coupler employed was one for the formation of the yellow image.

Instead of having the color coupler in the silver halide emulsion layer as shown in Examples 1 and 2, it is possible to have the color coupler present in one of the processing solutions, i.e., the filter layers of our invention are useful not only in photographic elements containing color couplers incorporated in the silver halide emulsion layer, which may be used for producing a negative or positive image according to known reversal techniques, but they can also be used in photographic elements intended for reversal color processing wherein the color couplers are present in one of the processing solutions, such as the color developer.

The following examples illustrate the manner of ob-

taining mordanted yellow filter layers directly by intermixing the yellow acid dye with the mordant, without the danger of forming objectionable precipitates.

## EXAMPLE 3

2.0 ccs. of a 10% aqueous solution of a  $\gamma$ -dimethylaminopropyl maleimide-styrene interpolymer, obtained as described in Example 1 of application Serial No. 663,810 were added to a 10% aqueous acetic acid solution which was, in turn, added to 20 ccs. of a 10% aqueous gelatin solution. To this mixture were then added successively, 3 ccs. of a 2% aqueous solution of dye 3, 0.5 cc. of a 7.5% aqueous solution of saponin, 0.4 cc. of a 0.27% aqueous solution of mucochloric acid and enough water to give 30 ccs. of solution. The mixture was then stirred for 5 minutes at 40° C. and coated on an ordinary cellulose acetate film base at a gelatin coverage of about 0.466 g. per square foot and a concentration of the dye at 0.014 g. per square foot. The coating was then washed under running water for 1 hour without any measurable loss of dye. Yet, immersion of the coating into a conventional photographic developer quickly removed the dye from the gelatin coating.

## EXAMPLE 4

In exactly the manner illustrated in Example 3 above, dye 4 was incorporated in a mordant layer containing the maleimide interpolymer. Washing of the coating for 1 hour under running water did not remove any measurable amount of dye yet the coating was quickly bleached by immersion in ordinary photographic color developer.

The yellow acid dye need not be dispersed directly in the silver halide emulsions as illustrated in Examples 1 and 2 above, but the emulsions can be first coated and the photographic element immersed in an aqueous solution containing the dye, sufficient quantity of dye being absorbed under these conditions. Subsequent treatment of the coated silver halide emulsion layer with a mordanted, undyed layer as described above, causes migration of the dye into the desired mordanted layer. Alternatively, the silver halide emulsion layer and/or the mordanted, undyed layer can be surface-coated with an aqueous solution of the desired yellow dye so that the dye then migrates into the mordanted layer. As indicated above, the dye need not be incorporated into the silver halide emulsion layer, but can be incorporated in one of the conventional hydrophilic colloid layers used as interlayers, and the dyed layer placed in contact with the mordanted, but undyed, layer.

It has also been found that the above-described mordants are particularly useful in color photography where it is desired to fix a competing coupler compound, such as those described in Weller et al. U.S. Patent 2,689,793, dated September 21, 1954, in one of the layers of a multi-layer element, such as in a particular light-sensitive silver halide emulsion layer. For example, these mordants can be used to fix a competing coupler, such as citrazinic acid or H-acid, in a photographic silver halide emulsion which is sensitive to a particular region of the spectrum. The silver halide emulsion layer contains one of the above-described mordants which fixes the competing coupler during the coating procedures customarily employed in preparing photographic color elements, yet allows the competing coupler to react with oxidized developer for the purpose of controlling color balance. This tends to increase sharpness of the final color image by allowing less oxidized developer to wander away from its desired place. If desired, the unused competing coupler can be removed by washing the finished element in an aqueous alkaline solution.

Our invention can be further illustrated by the accompanying drawings, in which FIG. 1 is a diagrammatic representation of the spectrophotometric curves of two of the mordanted filter layers of our invention and the spectrophotometric of Carey Lea silver. FIG. 2 is a

diagrammatic representation of one of the multi-layer color elements which embody the mordanted filter layers of our invention.

In FIG. 1, curve A represents the spectrophotometric curve of colloidal silver (i.e., Carey Lea silver) which is customarily employed in color photography; curve B represents the spectrophotometric curve of the filter layer illustrated in Example 1 above (i.e., tartrazine dispersed in the mordanted layer); and curve C represents the spectrophotometric curve of the filter layer illustrated in Example 2 above (i.e., dye 11 in the mordanted layer). It can be seen from FIG. 1 that the colloidal silver gives considerably less protection than the dyes of Examples 1 and 2 at wavelengths below 500 millimicrons and that the green density for the Carey Lea silver is higher than that of the dyes.

In FIG. 2 is depicted a multi-layer photographic element utilizing a mordanted filter layer obtained according to our invention. The multi-layer element comprises a support 10 having coated thereon a red-sensitive silver halide emulsion 11, a green-sensitive halide emulsion 12, a filter layer 14 containing  $\gamma$ -dimethylaminopropyl maleimide-styrene interpolymers and a yellow acid dye, such as dye 4 above, and finally a blue-sensitive silver halide emulsion layer 13. The multi-layer element can also contain other interlayers (not shown) such as gelatin layers, etc.

As indicated above, the filter dye can be incorporated in either the red- or green-sensitive emulsion layer which is in contact with the unsensitized colloid layer, such as layer 14 shown in FIGURE 2, instead of in the blue-sensitive layer as illustrated in the above examples. The following example will serve to illustrate the manner of incorporating the filter dye in the green-sensitive layer of a multi-color element of the type shown in FIGURE 2.

#### EXAMPLE 5

##### A. Control coating

A photographic element was prepared in the usual manner using a cellulose acetate film support. On the support was coated an ordinary gelatino-silver-bromide emulsion which had been red-sensitized and contained a coupler for the cyan image. Typical of the couplers which can be used are those described in Fierke et al. U.S. Patent 2,801,171, issued July 30, 1957, and Salminen et al. U.S. Patent 2,423,730, issued July 8, 1947. Over the red-sensitive emulsion was coated an ordinary gelatino-silver-bromide emulsion which had been green-sensitized and contained a coupler for the magenta image. Typical of the couplers which can be used are those shown in Loria et al. U.S. Patent 2,600,788, issued June 17, 1952. Over the green-sensitive coating, an ordinary colloidal silver layer was applied. Over the colloidal silver layer was coated an ordinary blue-sensitized gelatino-silver-bromide emulsion layer containing a coupler for the yellow image. Typical of the couplers which can be used are those shown in the McCrossen et al. application Serial No. 575,099, U.S. Patent 2,875,057, granted February 24, 1959, referred to above. Some or all of the above silver bromide emulsion layers can be gold and/or sulfur sensitized.

##### B. Filter dye coating

A multi-layer element of the type described in A above was prepared, except that dye 1 was incorporated in the green-sensitive emulsion layer at a coverage of about 16 mg. per square foot, and the colloidal silver layer was replaced with a mixture of gelatin (151 mg. per square foot) and a copolymer of styrene and  $\gamma$ -dimethylaminopropyl acrylamide (60 mg. per square foot). The filter dye (dye 1) was incorporated in the green-sensitive emulsion layer by dissolving it in methanol containing a small amount of triethanolamine, diluting the solution with water, and adding the aqueous solution directly to the green-sensitive layer. The gelatin layer containing the acrylamide resin

contained a small amount of hardener, such as mucchloric acid, and a spreading agent, such as saponin.

While the multi-layer coating of B of Example 5 above gave excellent color rendition and showed no detectable physical development, the multi-layer element described under A of Example 5 showed physical development and did not give as accurate color rendition as the element containing the mordanted filter dye.

Instead of using the acrylamide resin shown in Example 5 above, equally effective results were obtained using the same mordant described in Example 3 above. The use of the filter dye as an addendum to the green-sensitive emulsion, rather than to the blue-sensitive emulsion layer has the advantage that no detectable amount of dye can find its way into the blue-sensitive layer, and thus adversely affect the blue speed. The elements described in Example 5 can be processed in the usual manner, such as by the Kodak Ektachrome E-2 process.

The filter dyes useful in practicing our invention can be prepared according to known techniques. For example, the dyes represented by Formula IV can be prepared according to the method described in Brooker et al. U.S. Patents 2,493,747-8, issued January 10, 1950. An improved method of preparing certain sulfoalkyl dyes of the type represented by Formula IV above, is described in Brooker and Keyes U.S. application Serial No. 698,324, filed on even date herewith (now U.S. 2,917,516, granted December 15, 1959). For example, dye 2 above was prepared according to the method described in the Brooker and Keyes application, and was obtained as a crystalline solid melting at 293-4° C.

Dye 3 was prepared as follows:

#### EXAMPLE A

3 - (3,5 - disulfobenzamido) - 4[(3 - ethyl-2(3H)-benzoxazolydene)ethylidene] - 1 - phenyl - 2 - pyrazolin-5-one (dye 3)

A mixture of 2.58 g. (1 mol.) of 3-(3,5-disulfobenzamido)-1-phenyl-2-pyrazolin-5-one, di-potassium salt and 2.17 g. (1 mol.) of 2- $\beta$ -acetanilidovinyl-3-ethylbenzoxazolium iodide in 20 ml. of ethyl alcohol containing 0.55 g. (1 mol.+10% excess) of triethylamine was heated at the refluxing temperature for 20 minutes. After chilling, the dye was collected on a filter and washed with ethyl alcohol. The yield of crude dye as the di-potassium salt was 2.65 g. (77%). The dye was then dissolved in a small volume of water and a large excess of concentrated hydrochloric acid was added. After chilling, the dye was collected on a filter, washed with a little cold water and then recrystallized from water. The yield of twice recrystallized dye was 0.53 g. (17%) and the yellow crystals melted above 315° C.

In like manner 4-[(3-ethyl-2(3H)-benzoxazolydene)-ethylidene] - 3 - methyl-1-p-sulfophenyl-2-pyrazolin-5-one (dye 1) was prepared from 3-methyl-1-p-sulfophenyl-2-pyrazolin-5-one and 2- $\beta$ -acetanilidovinyl-3-ethylbenzoxazolium iodide. The yield of crude dye was 80%. The dye was purified by dissolving it, as the pyridine salt, in water, filtering the solution and then adding an excess of hydrochloric acid to the filtrate. After cooling, the dye was collected on a filter and washed with methyl alcohol. The yield of dye after two such treatments was 59% and the yellow crystals melted above 310° C.

The following examples describe the preparation of certain of the azo dyes useful in practicing our invention, although it is to be understood that other dyes are equally useful in our invention, and these dyes have been merely given as examples. As indicated above, the filter dyes of our invention can be used either in the form of a free acid, or in the form of their water-soluble alkali metal salts. Accordingly, no differentiation between acids, or salts of the acids, is made in the following examples.

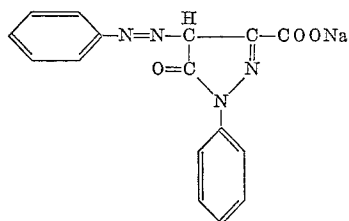


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2. A method according to claim 1 wherein said water-soluble dye contains a 5-pyrazolinone nucleus.

3. A method according to claim 1 wherein the water-soluble dye is tartrazine.

4. A method according to claim 1 wherein the water-soluble dye is a dye represented by the following formula:



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## References Cited in the file of this patent

## UNITED STATES PATENTS

1,954,294	Heymer	Apr. 10, 1934
2,548,564	Sprague	Apr. 10, 1951
2,882,156	Minsk	Apr. 14, 1959

## FOREIGN PATENTS

551,500	Great Britain	Feb. 25, 1943
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