

Oct. 18, 1960

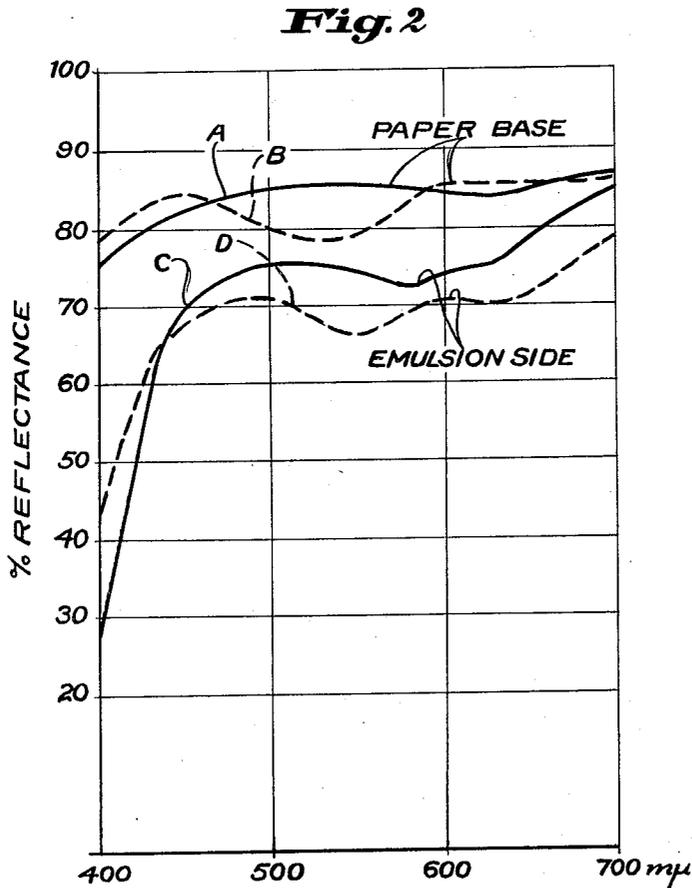
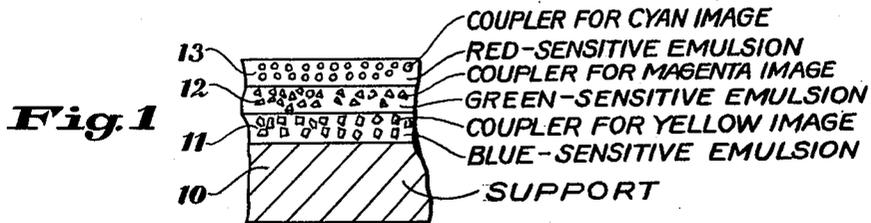
J. H. VAN CAMPEN

2,956,879

FILTER AND ABSORBING DYES FOR USE IN PHOTOGRAPHIC EMULSIONS

Filed Jan. 7, 1958

2 Sheets-Sheet 1



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2 Sheets-Sheet 2

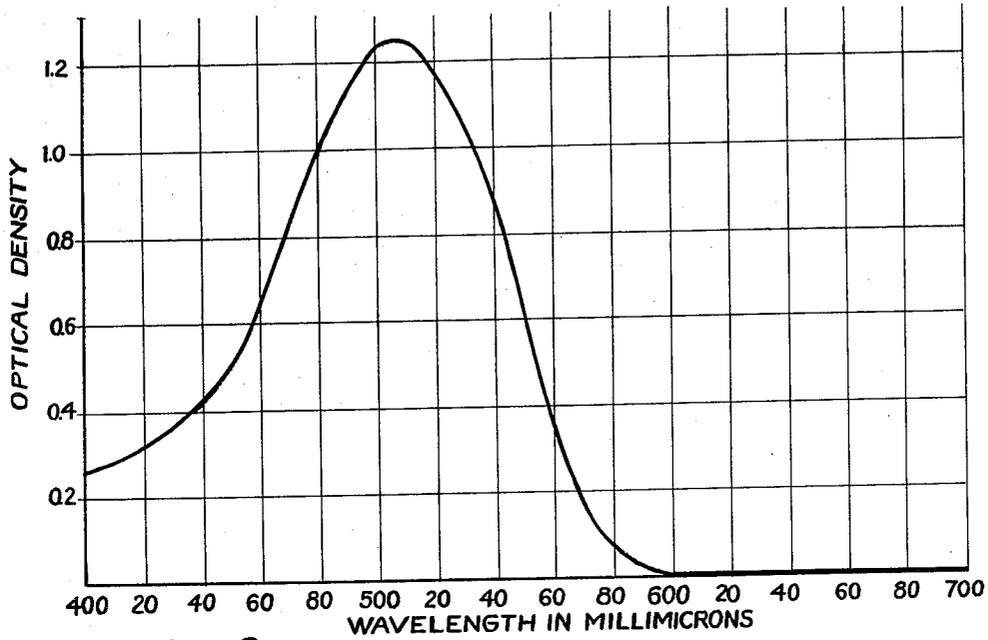


Fig. 3

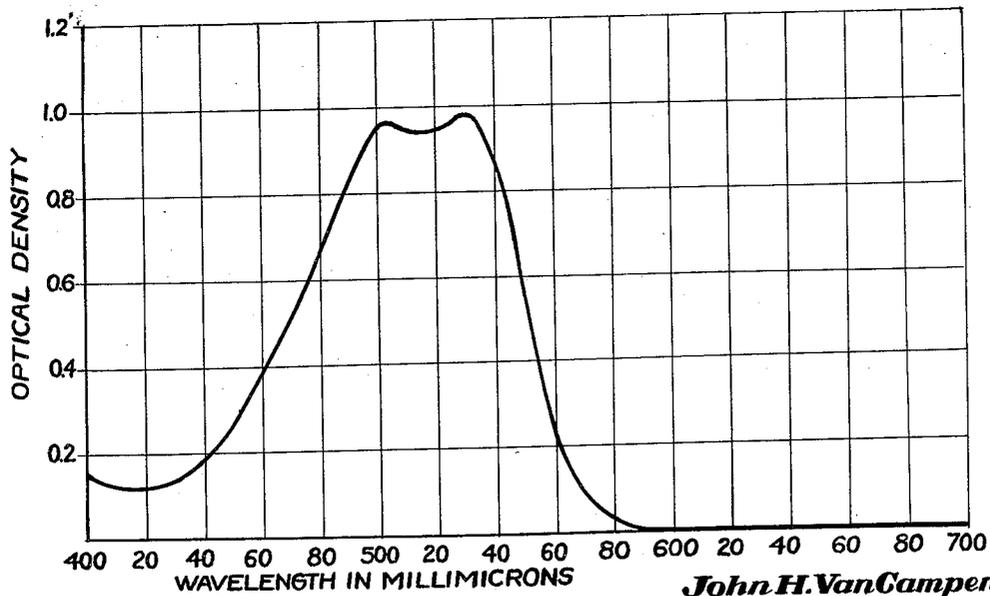


Fig. 4

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FILTER AND ABSORBING DYES FOR USE IN PHOTOGRAPHIC EMULSIONS

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This invention relates to photographic emulsions and photographic elements comprising such emulsions, and, more particularly, to such photographic products containing certain light-absorbing agents.

In certain photographic processes, and in particular those concerning color photography or reproduction of natural colors, the light-scattering caused by the silver halide grains creates considerable difficulty. For example, light which has been scattered by a given silver halide grain will travel until it strikes another silver halide grain where it is absorbed, thus making this latter silver halide grain developable. Of course, since this silver halide grain may not have been originally exposed, but received only secondary radiation, its development is not desired. In the past, it has been proposed to overcome this scattering effect by incorporating various dyes, other than optical or spectral sensitizing dyes, in the emulsions. While this practice might overcome to some extent the adverse effects of the light-scattering caused by the silver halide grains, other new difficulties are sometimes introduced. In some cases, these light-absorbing dyes leave residual stain, particularly where the silver halide emulsions have been coated upon a fibrous or paper base. This difficulty is particularly pronounced when continuous processing is used, which means that substantial quantities of sensitized materials are treated in the same photographic developer without removing solubilized materials which have a tendency to concentrate in the photographic developer. Of course, if the solubilized materials, including the light-absorbing dyes, which concentrate in the developer, can be removed during subsequent washing operations, no great harm is done. Frequently, however, these materials are not removed during subsequent operations so that they remain in the finished material as residual stain. Sometimes certain light-absorbing dyes give undesirable increases in background density, and even more serious in certain cases, a substantial loss in speed results due to the desensitizing effect of the dyes.

I have now found that a particular group of azonaphthalene dyes containing from 3 to 4 sulfo groups can advantageously be employed in photographic silver halide emulsions, and, in particular, green-sensitized silver halide emulsions, for the purpose of overcoming the difficulties mentioned above. The advantages of my invention are particularly outstanding in continuous processing of color materials comprising a fibrous or paper base.

It is, therefore, an object of my invention to provide photographic silver halide emulsions containing light-absorbing azonaphthalene dyes containing from 3 to 4 sulfo groups. Another object is to provide photographic silver halide emulsions optically or spectrally sensitized to the green region of the spectrum containing said azonaphthalene dyes. A further object is to provide photographic elements comprising said photographic silver halide emulsions. Still another object is to provide photographic elements for subtractive color photography comprising a plurality of photographic silver halide emul-

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sions, the sensitivity of which lies in different regions of the spectrum. Still another object is to provide photographic elements for color photography comprising a paper support which contains little or no residual stain after the photographic silver halide emulsions coated thereon have been processed in the customary manner. Other objects will become apparent from a consideration of the following description and examples.

The beneficial effect of the particular azonaphthalene dyes used in my invention is particularly evident in emulsions which are sensitive to green light, i.e., from about 500 to 600 m μ . Moreover, the particular dyes used in my invention appear to have little sensitizing or desensitizing effect upon the emulsions in which they are incorporated. This is evidenced by the fact that these dyes may tend to wander throughout all layers coated on the support, yet no serious desensitizing or sensitizing effects have been observed.

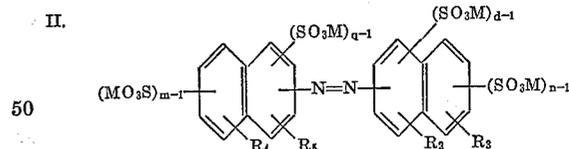
The azonaphthalene dyes useful in practicing my invention contain from 3 to 4 sulfo groups and have their maximum absorption in the region of the spectrum to which the photographic silver halide emulsion, to which they are added, is sensitive (which is generally the green region of the spectrum). Because of the sulfo substituent attached to the naphthalene rings, these dyes generally have a high degree of solubility in water.

By sulfo groups I mean the sulfonic acid group itself or water-soluble salts thereof, including alkali metal salts (e.g., sodium, potassium, etc.), ammonium salts (i.e., ammonium or organic ammonium, such as triethylammonium, pyridinium, triethanolammonium, etc.), etc.

Typical of the dyes which can be used in my invention are those represented by the following general formula:



wherein R and R₁ each represents a bi-nuclear aromatic group of the naphthalene series, said aromatic group containing at least one sulfo substituent, the total number of said sulfo substituents in the dyes represented by Formula I being from 3 to 4. A group of dyes embraced by Formula I above which can be used in my invention comprise the dyes represented by the following general formula:

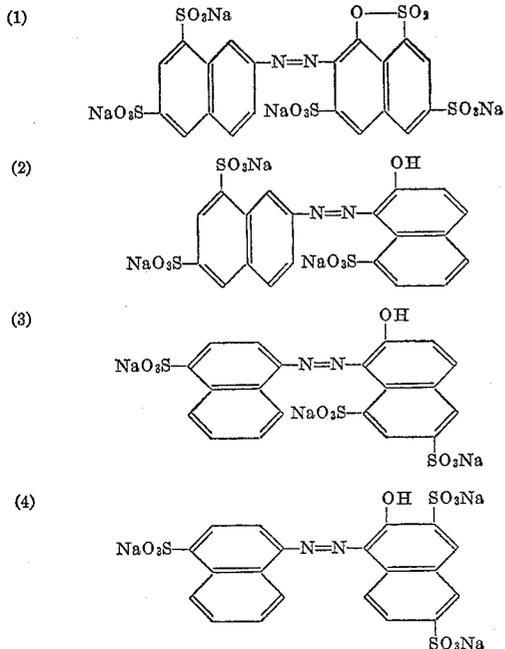


wherein R₂, R₃, R₄ and R₅ each represents a hydrogen atom, an alkyl group (e.g., methyl, ethyl, propyl, isopropyl, butyl, isobutyl, etc., especially an alkyl group containing from 1 to 4 carbon atoms), an alkoxy group (e.g., methoxyl, ethoxyl, etc.), a hydroxyl group, an amino group (e.g., amino, monoalkylamino, such as methylamino, ethylamino, etc., dialkylamino, such as dimethylamino, diethylamino, etc., acylamino, such as acetamido, propionamido, benzamido, etc.), an acyl group (e.g., acetyl, propionyl, etc.), a cyano group, etc., *d*, *m*, *n* and *q* each represents a positive integer of from 1 to 3, the sum of *d*, *m*, *n* and *q* being from 7 to 8, and M represents a hydrogen atom, an alkali metal atom or an ammonium radical as defined above with respect to the sulfo groups which must be present in my light-absorbing dyes. Especially useful dyes embraced by Formula II above are those dyes wherein R₂ or R₅ represents a hydroxyl group.

Specific dyes which can be employed in practicing my

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invention, which are embraced by the above general Formula I, include the following:



The above dyes can be prepared according to methods which have been previously described in the prior art. Dye 3 above is well-known as Schultz 213 and is sold commercially under such tradenames as Brilliant Scarlet 3R or Ponceau 4R Conc. It has the Color Index No. 185. Dye 4 above is well-known as Schultz 212 Dye.

The method of incorporating the azonaphthalene dyes of my invention in photographic silver halide emulsions is quite simple and can be effected merely by adding the solid dyes to the emulsions, although it is generally preferable to dissolve the dyes in an inert solvent, such as water, and disperse the dyes in the emulsions in the form of their solutions. Where the dye does not have sufficient solubility in water to perform the desired degree of light absorption, its solubility can be increased by adding a small amount of an organic solvent, such as pyridine, to the aqueous solvent. Alternatively, the dyes can be first dissolved in an organic solvent and then added to water prior to addition to the photographic emulsions. Since the dyes of my invention are generally characterized by a high degree of solubility in water, it is usually not necessary to resort to any particular technique in order to disperse the dyes uniformly throughout the emulsions. In general, I prefer to add the dyes directly to the finished, washed emulsions in the form of their aqueous (neutral) solutions. If desired, the emulsions can be digested for a short time before coating.

The quantity of azonaphthalene dye employed in my invention can be varied, depending upon the particular emulsion used, the concentration of silver halide, effects desired, etc. In general, I have found that from about 0.5 to 5.0 mg. of dye/ft.² of coated emulsion is quite adequate for the purposes of my invention. Based on the quantity of silver halide in the emulsion, I have found that from about 0.5 to about 10 grams of dye per gram mole of silver can be employed, although larger or smaller amounts of dye can be used, depending upon the particular conditions, some of which are mentioned above.

The photographic silver halide emulsions employed in my invention can be optically sensitized or unsensitized. The usual optical sensitizing dyes can be used, such as the cyanines, merocyanines, complex (trinuclear) cyanines, complex (trinuclear) merocyanines, styryls, hemicyanines, etc. These dyes can contain the usual basic

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nuclei, such as thiazole, benzothiazole, naphthothiazole, benzoxazole, naphthoxazole, benzoselenazole, naphthoselenazole, quinoline, etc., or in the case of the merocyanine dyes, such nuclei as rhodanine, 2-thiohydantoin, oxazolidione, pyrazolone, etc. Such dyes, for example, are described in Brooker U.S. Patent 2,185,182, dated January 2, 1940; Brooker U.S. Patent 2,241,237, dated May 6, 1941; Carroll U.S. Patent 2,635,961, dated April 21, 1953; Carroll U.S. Patent 2,652,330, dated September 15, 1953; Heseltine and Brooker U.S. Patent 2,666,761, dated January 19, 1954; Carroll and Jones U.S. Patent 2,704,715, dated March 22, 1955; etc. In general, the particular azonaphthalene dye used should have its maximum absorption in the same spectral region to which the sensitizing dye sensitizes the emulsion.

My invention is primarily directed to the ordinarily employed silver halide developing-out emulsions, e.g., gelatino-silver-chloride, -chlorobromide, -chloriodide, -chlorobromiodide, -bromide and -bromiodide developing-out emulsions. Particularly useful results have been obtained with gelatino-silver-chloro-bromide emulsions which are useful in preparing subtractive color reproductions on fibrous or paper supports. Emulsions which form the latent image mostly inside the silver halide grains, such as the emulsions set forth in Knott and Stevens U.S. Patent 2,456,956, dated December 21, 1948, can also be employed in practicing my invention.

While my invention is particularly directed to the ordinarily employed gelatino-silver-halide emulsions, carriers other than gelatin, e.g., a resinous substance, such as polyvinyl alcohol, or cellulosic material, such as hydrolyzed cellulose acetate, which has no deteriorating effect upon the light-sensitive silver salt materials, can be employed.

The emulsions prepared in accordance with my invention can be coated in the usual manner upon any suitable support, e.g., glass, cellulose nitrate film, cellulose acetate film, polyvinyl acetal resin film, polycarbonate film, polystyrene film, polyester film, metal, etc., although I have found that the advantages of my invention are particularly outstanding when the support is paper or some other fibrous material which is more likely to absorb stain than hydrophobic film materials. Since the emulsions themselves also tend to absorb soluble developer components and decomposition products, it is to be understood that the advantages of my invention also extend to film materials or other hydrophobic supports, although the results are not as outstanding in these instances.

Photographic silver halide emulsions, such as those listed above, can also contain such addenda as chemical sensitizers, e.g., sulfur sensitizers (e.g., allyl thiocarbamide, thiourea, allylthiocyanate, cystine, etc.), various gold compounds (e.g., potassium chloroaurate, auric trichloride, etc.) (see Baldisiefen U.S. Patent 2,540,085, dated February 6, 1951; Damschroder U.S. Patent 2,597,856, dated May 27, 1952; and Yutzy and Leermakers U.S. Patent 2,597,915, dated May 27, 1952), various palladium compounds, such as palladium chloride (Baldisiefen et al. U.S. Patent 2,540,086, dated February 6, 1951), potassium chloropalladate (Stauffer and Smith U.S. Patent 2,598,079, dated May 27, 1952), etc., or mixtures of such sensitizers; antifoggants, such as ammonium chloroplatinate (Trivelli and Smith U.S. Patent 2,566,245, dated August 28, 1951), ammonium chloroplatinate (Trivelli and Smith U.S. Patent 2,566,263, dated August 28, 1951), benzotriazole, nitrobenzimidazole, 5-nitroindazole, benzidine, mercaptans, etc. (see Mees, "The Theory of the Photographic Process," Macmillan Pub., 1942, page 460), or mixtures thereof; hardeners, such as formaldehyde or chrome alum (Miller U.S. Patent 1,763,533, dated June 10, 1930), glyoxal (Brunken U.S. Patent 1,870,354, dated August 9, 1932), dibromacrolein (Bloch et al. British Patent 406,750, accepted March 8, 1934), etc.; color couplers, such as those described in Salminen

and Weissberger U.S. Patent 2,423,730, dated July 8, 1947, Spence and Carroll U.S. Patent 2,640,776, dated June 2, 1953, etc.; or mixtures of such addenda. Dispersing agents for color couplers, such as those set forth in Jelley and Vittum U.S. Patent 2,322,027, dated June 15, 1943 and Mannes and Godowsky U.S. Patent 2,304,940, dated December 15, 1942, can also be employed in the above-described emulsions.

The following example will serve to illustrate the beneficial effect of the azonaphthalene dyes of my invention as compared with a closely-related azo dye which has been used previously for the same purpose. This example illustrates that there is much less speed loss in the green region of the spectrum using the dyes of my invention than results when a closely-related dye is used for light-absorbing purposes.

EXAMPLE 1

To different portions of the same batch of photographic gelatino-silver-chlorobromide emulsion (green sensitized) containing a coupler for the magenta image, such as one of the pyrazolone couplers described in Loria et al. U.S. Patent 2,600,788, dated June 17, 1952 (e.g., 3-{3'-I(2'', 4''-di-tert. amylphenoxy)acetamido]benzamido}-1-(2',4', 6'-trichlorophenyl)-5-pyrazolone) was added an azonaphthalene dye, as identified in Table I (Dye 3), the amounts used being given as mg./ft.² of the coated emulsions. The emulsions were then digested for a short time and coated on a paper support, chill set and dried. A second series of photographic gelatino-silver-chlorobromide emulsions was treated with a different light-absorbing dye, Azorhodine 2G, in the amounts given in the table (mg./ft.²) and the emulsions digested for a short time, coated on a paper support, chill set and dried. Each of the series of coated emulsions was then exposed in an intensity scale sensitometer using 3000° K.-500 watt illumination from a projection incandescent lamp. The exposed emulsions were then processed in a developer having the following composition:

Water	liter	1.0
Benzyl alcohol	cc	12.6
Sodium hexametaphosphate (Calgon)	grams	2.0
Sodium sulfite, anhydrous	do	2.1
Sodium carbonate monohydrate	do	26.8
Sodium bicarbonate	do	2.9
Potassium bromide	do	0.48
Sodium chloride	do	0.7
Hydroxylamine sulfate	do	2.1
Color developer *	do	4.2
(pH at 75° F.)		9.96

* 4-amino-N-ethyl-N-(β-methanesulfonamidoethyl)-m-toluidine sesquisulfate monohydrate.

The developed coatings were then immersed in a stop bath for about 2 minutes. The stop bath had the following composition:

Water	liter	1.0
Glacial acetic acid	cc	17.0
Sodium sulfite, anhydrous	grams	20.0

The coatings were then fixed for 2 minutes in a bath having the following composition:

Water	liter	1.0
Sodium thiosulfate	grams	223
Sodium bisulfite	do	12.0
Sodium acetate, anhydrous	do	14.0
Sodium citrate	do	1.7
Boric acid	do	5.0
Potassium alum, granular	do	24.0

The coatings were then washed in running water at about 73 to 77° F. for 2 minutes. The paper coatings

were then treated for 4 minutes at 73° to 77° F. in a bleach bath having the following composition:

Water	liter	1.0
Sodium nitrate	grams	45.0
Potassium ferricyanide	do	22.5
Potassium bromide	do	8.2
Boric acid	do	7.5
Borax	do	0.97

The paper coatings were then washed in running water at 73° to 77° F. for 2 minutes and then fixed for 2 minutes in a hardener-fixing bath having the following composition:

Water	liter	1.0
Glacial acetic acid	cc	15
Sodium zirconyl sulfate (Zirconan-N)	grams	0.46
Sodium bisulfite	do	17.9
Sodium thiosulfate	do	167.7
Sodium citrate	do	2.5
Boric acid	do	7.2
Potassium alum, granular	do	35.5
Sodium hydroxide, granular	do	10.4
Zinc sulfate monohydrate	do	7.5

The paper coatings were then washed in running water at 73° to 77° F. for 8 minutes and then treated for 3 minutes in a hardening bath at 73° to 77° F., the bath having the following composition:

Water	liter	1.0
Sodium hexametaphosphate (Calgon)	grams	0.75
Sodium carbonate monohydrate	do	8.8
Formaldehyde (37% by weight)	ccs	25.5

The paper coatings were then washed for 2 minutes in running water and treated for 3 minutes in a buffer bath having the following composition:

Water	liter	1.0
Citric acid	grams	30.0
Borax	do	20.4

The prints were then allowed to dry in the air or in a conventional drier.

The speeds of the coatings obtained above were then read on a curve tracing reflection densitometer which read the curves of monochromatic density as a function of exposure. A Perkin-Elmer Monochromator, Model 83, equipped to emit 596 mμ radiation, was used as a light source. The speed figures are given in the following table in terms of log E units. The control coating had a green density in the shoulder region of the curve of about 1.40, in the toe region a density of about 0.06 and fresh magenta stain of about 0.10. The coatings containing the light-absorbing dyes had density values approximately the same as the control coating, insofar as the shoulder and toe regions of the curve and stain were concerned. Of course, it is to be understood that these figures were obtained from a single run and that the stain level had no opportunity to build up as would occur in a continuous process.

Table I

Coating	Addenda	Conc. (mg./ft. ²)	Fresh Speed	
			Green	Δ log E
(a)	none		1.06	0
(b)	Dye 3	1	.94	-.12
(c)	do	2	.80	-.26
(d)	do	3	.71	-.35
(e)	do	4	.63	-.43
(f)	Azorhodine 2G	1	.80	-.26
(g)	do	2	.62	-.44
(h)	do	3	.50	-.56
(i)	do	4	.40	-.66

My invention can be further illustrated by reference to the accompanying drawings, in which:

Figure 1 is a diagrammatic, cross-sectional view of a multilayer color element which can be advantageously processed according to my invention,

Figure 2 is a reproduction of a set of reflectance curves showing the advantages of using the light-absorbing dyes of my invention over a structurally-related dye,

Figure 3 is a reproduction of the spectrophotometric curve of pure Schultz 213 Dye, and

Figure 4 is a reproduction of the spectrophotometric curve of a dye, Azorhodine 2G, which is structurally related to the dyes of the instant invention.

In Figure 1, there is shown in cross-sectional view, a photographic color element of the type which can be advantageously employed in my invention. The element comprises a support 10, which can be composed of any conventional material, such as those listed above, and a blue-sensitive silver halide emulsion layer 11 coated on top of this support. The blue-sensitive emulsion can contain a coupler or color-forming compound which reacts with the oxidation products of the color developer to produce a yellow image. Coated on top of the blue-sensitive layer is a green-sensitive silver halide emulsion layer 12, which can contain a coupler or color-forming compound capable of coupling with the oxidation products of the color developer to produce a magenta image. The element shown has an outermost red-sensitive silver halide emulsion layer 13, which is coated on top of the green-sensitive emulsion. This red-sensitive emulsion can contain a coupler or color-forming compound capable of coupling with the oxidation products of a color developer to produce a cyan image. The photographic support illustrated in Figure 1 can, if desired, contain interlayers (not shown), such as gelatin interlayers, filter layers, etc.

As indicated above, the advantages of my invention are particularly outstanding in the continuous processing of multilayer color elements, which involves large quantities of sensitized stock and prolonged use of the same developing baths. Under such rigid conditions, it is obvious that the quantity of soluble materials in the sensitized stock will approach an equilibrium with the soluble materials in the developing baths. Consequently, it is to be expected that the quality of the processed materials will fall off rapidly if some control is not exercised over the processing. I have found that the dyes of my invention are markedly superior to dyes which have been customarily used in the prior art in the green-sensitive layers of color elements, particularly from the standpoint of less desensitization and stain (both with respect to the emulsions themselves and the paper supports which are frequently used for print materials). The advantages of my invention with respect to stain level are illustrated in the following example.

EXAMPLE 2

Part (a).—A photographic 3-layer material similar to the type illustrated in Figure 1 was continuously processed until the amount of light-absorbing dye in the color developer reached a maximum. The multilayer element comprised a support having coated thereon an ordinary gelatino-silver-chlorobromide emulsion which was blue-sensitive and contained a coupler for the yellow image of the type described in McCrossen et al. U.S. application Serial No. 575,099, filed March 30, 1956 (now U.S. Patent 2,875,057, issued February 24, 1959). The blue-sensitive layer also contained conventional emulsion addenda, such as an anti-stain agent (e.g. 2-n-octadecyl-5-(2-sulfo-tert. butyl)hydroquinone potassium salt, etc.), etc. Coated over the blue-sensitive layer was an ordinary gelatin interlayer. Over this gelatin interlayer was coated an ordinary gelatino-silver-chlorobromide emulsion which was green-sensitive and contained a coupler for the magenta image, such as one of the couplers

described in Loria et al. U.S. Patent 2,600,788, dated June 17, 1952. The coupler was disposed in a conventional coupler solvent, such as tricresylphosphate. The green-sensitive emulsion layer also contained an anti-stain agent, such as dioctylhydroquinone. The green-sensitive emulsion layer also contained a quantity of Schultz 213 Dye sufficient to give a coverage of 3.0 mg./ft.² of coating.

Over the green-sensitive layer was coated an ordinary gelatin layer containing an ultra-violet absorbing compound, such as one of the compounds described in Sawdey U.S. Patent 2,739,888, dated March 27, 1956. Also, the gelatin filter layer contained dioctylhydroquinone dispersed in a solvent, such as tricresylphosphate. Over the gelatin filter layer was coated an ordinary gelatino-silver-chlorobromide emulsion which was red-sensitive. This red-sensitive emulsion contained a coupler for the cyan image, such as one of the couplers described in Fierke U.S. Patent No. 2,801,171, dated July 30, 1957, the couplers being dispersed in a conventional solvent, such as dibutyl phthalate. The red-sensitive emulsion also contained an anti-stain agent, such as dioctylhydroquinone, and a red-light absorbing dye of the type described in Saunders and Wilson U.S. application Serial No. 541,059, filed October 17, 1955 (now U.S. Patent 2,865,752, issued December 23, 1958). Over the red-sensitive layer was coated an ordinary gelatin protective layer.

The above element was exposed in the customary manner to a subject and the exposed coatings processed in the same processing baths described above in Example 1. A total of 1800 square feet of coating was processed over a period of 24 hours. The developer composition was then analyzed and the decomposition products contained therein measured by means of a spectrometer using 302 m μ radiation. The results of the analysis are given in Table II below, where the coating is identified as element A.

Part (b).—A second series of coatings was run in the manner described above for element A, except that the green-sensitive layer of the color element contained 3.0 mg./ft.² of Azorhodine 2G light-absorbing dye in place of the Schultz 213 Dye used in Part (a). After a total of 2250 square feet of coating had been processed over a period of 30 hours, the concentration of the Azorhodine 2G in the color developer was at a maximum. The manner of processing the coating was exactly the same as that described in Example 1 above. The developer composition was then analyzed as under Part (a) above. The element used under Part (b) is identified as element B in the table. The composition of the seasoned developers was as follows:

Table II

Ingredient	Element A	Element B
Benzyl Alcohol.....cc.	11.3	11.5
Sodium Sulfite.....g.	2.15	2.25
Sodium Bromide.....g.	0.77	0.5
Sodium Chloride.....g.	0.84	0.75
Color Developer.....g.	3.30	3.70
Decomposition Products.....g.	0.80	0.90
Relative Total Alkalinity.....	22.8	22.5
Green Absorber Dye.....g.	.023	.025

The specific gravity of the developer composition after seasoning the element A was 1.031 against 1.033 for element B. The pH of the seasoned developer for element A was 9.90 against 9.98 for element B.

The residual stain in the coatings obtained in Example 2 above was determined both for the emulsion side of the coatings and for the paper base. In Figure 2 of the accompanying drawings are shown the results obtained. The percentage reflectance is plotted as a function of the wavelength of incident light upon the paper base and the emulsions. In Figure 2, curve A represents

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the reflectance of the paper base of element A, while curve B (dotted line) represents the reflectance of the paper base of element B. It is quite apparent that there is considerable stain present in element B as compared with element A, particularly in the green region. In Figure 2, curve C represents the reflectance of the emulsion side of element A, while curve D (dotted line) represents the reflectance of the emulsion side of element B. Again, it is evident that element B has considerable residual stain as compared with element A.

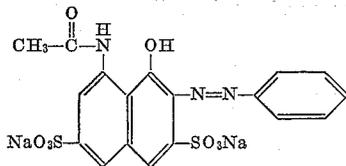
In the accompanying drawings, Figure 3 is a reproduction of the spectrophotometric curve of pure Schultz 213 Dye, the density of the dye being plotted as a function of the wavelength.

In Figure 4, there is shown a reproduction of the spectrophotometric curve of Azorhodine 2G Dye, the density being plotted as a function of the wavelength.

Azorhodine 2G Dye has the Color Index No. 31 and can be prepared according to conventional techniques. Dye 1 above was prepared in the same manner as Schultz VII-226, except that diazotized 2-naphthylamine-6,8-disulfonic acid was coupled with an equimolar amount of 1,8-naphthosultone-3,6-disulfonic acid in alkaline solution (instead of with salicylic acid as for Schultz VII-226). In like manner, Dye 2 above was prepared, except that 1 mole of 2-naphthol-8-sulfonic acid was used in place of the salicylic acid used to prepare Schultz VII-226.

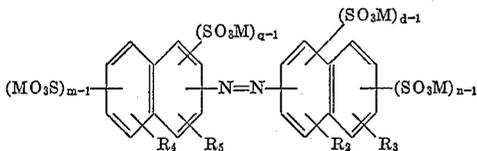
The term "sulfo" as used in the foregoing specification and in the following claims is intended to include the free sulfonic acid group, as well as water-soluble salts of this group, such as sodium, potassium, ammonium, organic ammonium (e.g., pyridinium, triethylammonium, triethanolammonium, etc.), etc.

Azorhodine 2G, used in Examples 1 and 2 above, can be represented by the following formula:



I claim:

1. A photographic gelatino-silver-halide emulsion optically sensitized to the green-light region of the spectrum containing from about 0.5 to 10 grams per mole of silver halide of a water-soluble azo dye selected from those represented by the following general formula:

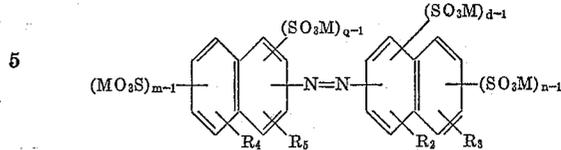


wherein R_2 , R_3 , R_4 and R_5 each represents a member selected from the group consisting of a hydrogen atom and a hydroxyl group, d , m , n and q each represents a positive integer of from 1 to 3, the sum of d , m , n and q being from 7 to 8, and M represents a member selected from the group consisting of a hydrogen atom, an alkali metal atom, and an ammonium radical, said azo dye having its maximum absorption in the green-light region of the spectrum.

2. A photographic gelatino-silver-halide emulsion optically sensitized to the green-light region of the spectrum containing (1) a color-forming compound capable of coupling with the oxidation products of a color developer to provide a magenta image and (2) from about 0.5 to 10 grams per mole of silver halide of an azo

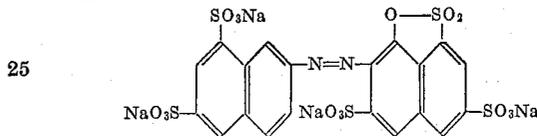
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dye selected from those represented by the following general formula:

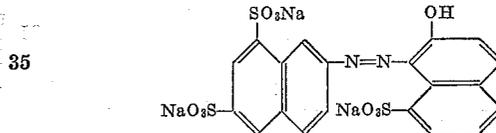


wherein R_2 , R_3 , R_4 and R_5 each represents a member selected from the group consisting of a hydrogen atom and a hydroxyl group, d , m , n and q each represents a positive integer of from 1 to 3, the sum of d , m , n and q being from 7 to 8, and M represents a member selected from the group consisting of a hydrogen atom, an alkali metal atom, and an ammonium radical, said azo dye having its maximum absorption in the green-light region of the spectrum.

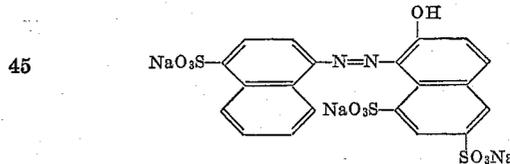
3. A green-sensitized photographic silver halide emulsion containing from about 0.5 to 10 grams per mole of silver halide of the dye represented by the following formula:



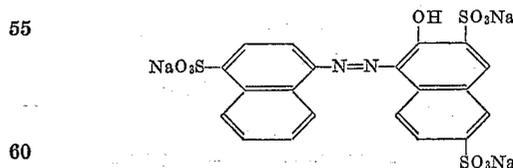
4. A green-sensitized photographic silver halide emulsion containing from about 0.5 to 10 grams per mole of silver halide of the dye represented by the following formula:



5. A green-sensitized photographic silver halide emulsion containing from about 0.5 to 10 grams per mole of silver halide of the dye represented by the following formula:



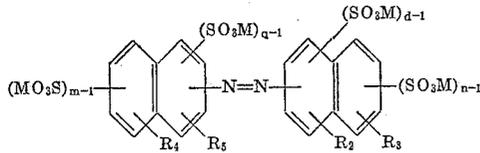
6. A green-sensitized photographic silver halide emulsion containing from about 0.5 to 10 grams per mole of silver halide of the dye represented by the following formula:



7. A photographic element for subtractive color photography comprising a support having coated thereon a plurality of silver halide emulsion layers, one of which is sensitive to the blue region of the spectrum and contains a color-forming compound capable of coupling with the oxidation products of a color developer to produce a yellow image, one of which is sensitive to the red region of the spectrum and contains a color-forming compound capable of coupling with the oxidation products of a color developer to produce a cyan image and one of which is sensitive to the green region of the spectrum and contains (1) a color-forming compound capable of coupling with the oxidation products of a color developer to produce a magenta image and (2) from

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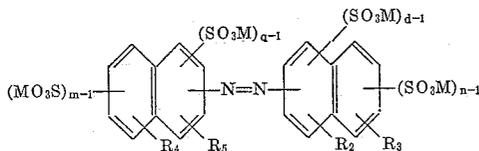
about 0.5 to 10 grams per mole of silver halide of a water-soluble azo dye selected from those represented by the following general formula:



wherein R_2 , R_3 , R_4 and R_5 each represents a member selected from the group consisting of a hydrogen atom and a hydroxyl group, d , m , n and q each represents a positive integer of from 1 to 3, the sum of d , m , n and q being from 7 to 8, and M represents a member selected from the group consisting of a hydrogen atom, an alkali metal atom, and an ammonium radical, said azo dye having its maximum absorption in the green-light region of the spectrum.

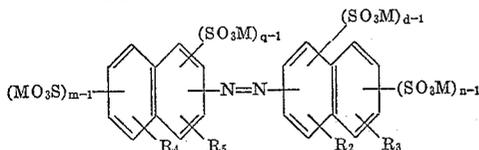
8. A photographic element according to claim 7 wherein the support is paper and the silver halide emulsion layer closest to the paper support is a blue-sensitive silver halide emulsion layer, the silver halide emulsion layer farthest from the paper support is a red-sensitive silver halide emulsion layer and the green-sensitive silver halide emulsion layer lies between the red-sensitive silver halide emulsion layer and the blue-sensitive silver halide emulsion layer.

9. A photographic gelatino-silver-chlorobromide emulsion optically sensitized to the green-light region of the spectrum containing from about 0.5 to 10 grams per mole of silver chlorobromide of a water-soluble azo dye selected from those represented by the following general formula:



wherein R_2 , R_3 , R_4 and R_5 each represents a member selected from the group consisting of a hydrogen atom and a hydroxyl group, d , m , n and q each represents a positive integer of from 1 to 3, the sum of d , m , n and q being from 7 to 8, and M represents a member selected from the group consisting of a hydrogen atom, an alkali metal atom, and an ammonium radical, said azo dye having its maximum absorption in the green-light region of the spectrum.

10. A photographic gelatino - silver - chlorobromide emulsion optically sensitized to the green-light region of the spectrum containing (1) a color-forming compound capable of coupling with the oxidation products of a color developer to provide a magenta image and (2) from about 0.5 to 10 grams per mole of silver chlorobromide of an azo dye selected from those represented by the following general formula:



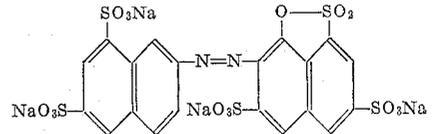
wherein R_2 , R_3 , R_4 and R_5 each represents a member selected from the group consisting of a hydrogen atom and a hydroxyl group, d , m , n and q each represents a

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positive integer of from 1 to 3, the sum of d , m , n and q being from 7 to 8, and M represents a member selected from the group consisting of a hydrogen atom, an alkali metal atom, and an ammonium radical, said azo dye having its maximum absorption in the green-light region of the spectrum.

11. A photographic silver halide developing-out emulsion optically sensitized to the green-light region of the spectrum containing (1) a color-forming compound capable of coupling with the oxidation products of a color developer to provide a magenta image, and (2) from about 0.5 to 10 grams per mole of silver halide of an azo dye represented by the following formula:

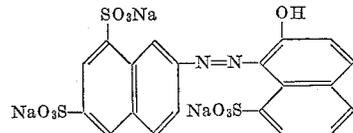
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12. A photographic silver halide developing-out emulsion optically sensitized to the green-light region of the spectrum containing (1) a color-forming compound capable of coupling with the oxidation products of a color developer to provide a magenta image, and (2) from about 0.5 to 10 grams per mole of silver halide of an azo dye represented by the following formula:

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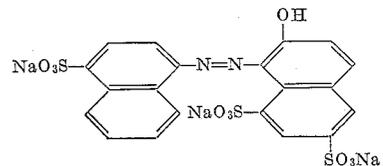


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13. A photographic silver halide developing-out emulsion optically sensitized to the green-light region of the spectrum containing (1) a color-forming compound capable of coupling with the oxidation products of a color developer to provide a magenta image, and (2) from about 0.5 to 10 grams per mole of silver halide of an azo dye represented by the following formula:

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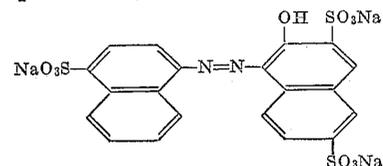


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14. A photographic silver halide developing-out emulsion optically sensitized to the green-light region of the spectrum containing (1) a color-forming compound capable of coupling with the oxidation products of a color developer to provide a magenta image, and (2) from about 0.5 to 10 grams per mole of silver halide of an azo dye represented by the following formula:

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