

1

2

3,582,338

FILM ELEMENTS AND PROCESS OF PREPARING SAME USING ELECTRON BOMBARDMENT

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16 Claims

ABSTRACT OF THE DISCLOSURE

Photographic elements are prepared by spectrally sensitizing a photographic silver halide emulsion with a cationic imidazolocyanine dye; incorporating a photographic color former in said emulsion; subjecting a hydrophobic surface to sufficient electron bombardment to provide good adhesion for said emulsion; and, coating said emulsion over the hydrophobic surface substantially immediately after electron bombardment. Photographic elements are provided comprising an electron bombarded hydrophobic support having coated thereon an emulsion spectrally sensitized with a cationic imidazolocyanine dye, and containing photographic color former.

This invention relates to a method for preparing photographic elements, and more particularly to a method for preparing spectrally sensitized photographic elements which are coated on hydrophobic surfaces. It also relates to novel photographic elements.

It is well known that photographic silver halide emulsions can be coated on supports having a hydrophobic surface. One highly useful photographic support is polyolefin coated paper, the polyolefin being the hydrophobic surface. Such supports offer considerable advantages over prior art paper supports in that the polyolefin acts as an efficient barrier between the emulsion and various contaminants or materials which can be contained in the paper. The polyolefin prohibits such contaminants from exerting adverse effects on the emulsion. In addition, paper supports which have polyolefin coatings on both sides are effectively waterproofed.

Photographic substrates having a hydrophobic surface, such as a polyolefin surface, require some treatment in order to obtain sufficient adhesion between the hydrophobic surface and the photographic silver halide emulsion. One of the most convenient techniques for obtaining sufficient adhesion is to electron bombard the hydrophobic surface. Electron bombardment is also known as corona discharge treatment. Processes for electron bombarding hydrophobic surfaces are described in Alsup and Venor British Patents 971,058 and 1,060,526 (polyolefin surfaces); Carroll et al. U.S. Patent 3,220,842, issued Nov. 30, 1965 [poly(ethylene terephthalate)]; and, Crawford et al. U.S. Patent 3,117,865, issued Jan. 14, 1964 (paper coated with chromium halide complex, such as sterato chromic chloride).

The use of electron bombarded hydrophobic surfaces for photographic silver halide emulsions containing a color former has presented a problem in color photography. Spectrally sensitized silver halide emulsions containing color former coated on a hydrophobic surface which has been electron bombarded have produced mottled dye images.

The problem of dye mottle with silver halide emulsions containing color former which are coated on electron bombarded hydrophobic surfaces appears to be most severe for a short period of time, such as up to about one hour, after electron bombardment. Mottle is not as severe if spectrally sensitized emulsions containing color former

are coated on the electron bombarded hydrophobic surface a considerable time (e.g., 24 to 36 hours) after the electron bombardment treatment. Although a holding period avoids mottle, it introduces serious disadvantages in manufacturing operations. Thus, the support must be stored after electron bombardment for a sufficient time to avoid mottle, but the emulsion must be coated on the support within about 24 to 36 hours after electron bombardment to obtain adequate emulsion adhesion.

There is a need, therefore, for a process whereby spectrally sensitized photographic silver halide emulsions containing color former can be coated on a hydrophobic surface substantially immediately after the surface has been electron bombarded.

One object of this invention is to provide novel photographic elements and processes for the preparation of such elements.

Another object of this invention is to provide a novel process for preparing light sensitive photographic elements which have a spectrally sensitized photographic silver halide emulsion layer containing color former coated on an electron bombarded hydrophobic surface.

A further object of this invention is to provide a method for coating spectrally sensitized silver halide emulsions containing color former on an electron bombarded hydrophobic surface whereby mottle-free dye images can be obtained.

Still another object of this invention is to provide a method for coating spectrally sensitized light sensitive silver halide emulsions containing color former onto an electron bombarded hydrophobic surface without undue photographic speed loss.

Other objects of this invention will be apparent from the disclosure herein and the appended claims.

In accordance with one embodiment of this invention, light sensitive photographic elements are prepared by the method which comprises:

- (1) spectrally sensitizing a light sensitive photographic silver halide emulsion with a cationic imidazolocyanine dye;
- (2) incorporating photographic color-former in said emulsion;
- (3) electron bombarding a hydrophobic surface to provide good adhesion for said emulsion; and,
- (4) coating said emulsion onto said hydrophobic surface substantially immediately after said electron bombardment treatment.

In another embodiment of this invention, novel photographic elements are provided which comprise a support which has an electron bombarded hydrophobic surface, and a photographic silver halide emulsion coated thereover spectrally sensitized with an imidazolocyanine dye, and containing photographic color former.

Spectral sensitization of photographic silver halide emulsions with a cationic imidazolocyanine dye allows the preparation of photographic elements by coating an emulsion containing color former onto a hydrophobic surface substantially immediately after it has been electron bombarded. Photographic elements prepared in accordance with this invention are free from mottle and do not exhibit speed loss.

The process of this invention can be carried out by spectrally sensitizing photographic silver halide emulsions with a cationic imidazolocyanine dye of the type used to spectrally sensitize silver halide emulsions.

As used herein and in the appended claims, "imidazolocyanine" dyes refers to those dyes which have the amidinium ion chromophoric system (see Mees and James, "The Theory of the Photographic Process," page 201, 3rd. edition, 1965, published by the MacMillan Com-

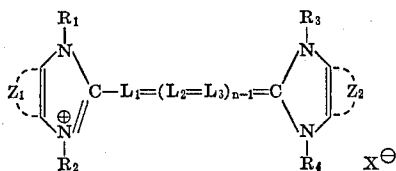
3

pany, New York) and which feature two imidazole nuclei joined together by a polyene chain containing an equal number of alternating single and double bonds, the terminal carbon atoms of the polyene chain being the "2" carbon atom of the respective imidazole nuclei. The imidazole nuclei can have an aryl group fused thereto, such as a benzo group or a naphtho group (i.e., a benzimidazole nucleus or a naphthimidazole nucleus). The preferred imidazole nuclei are the benzimidazole nuclei and naphthimidazole nuclei.

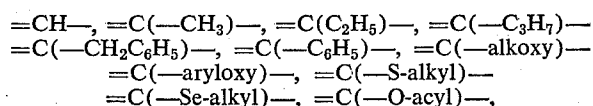
The term "cyanine" is used herein to include monomethine cyanines as well as polymethine cyanines, e.g., carboyanines and dicarboyanines.

The term "cationic" as used herein excludes betaine type dyes and anionic dyes (e.g., disulfoalkyl substituted cyanine dyes). Preferably, the imidazolocyanine dyes are free from any group which is as acidic, or which is more acidic than carboxy, e.g., sulfo or sulfato.

A highly useful class of cationic imidazolocyanine dyes are represented by the following formula:



wherein Z_1 and Z_2 each represents the atoms necessary to complete an aryl group, such as a benzo group or a naphtho group, which aryl group can be substituted with various groups, including chloro, fluoro, bromo, cyano, alkyl (such as methyl, ethyl, propyl, butyl, trifluoromethyl, benzyl, phenethyl, etc.), or aryl, such as phenyl, tolyl, naphthyl, methoxyphenyl, chlorophenyl, etc.; L_1 , L_2 and L_3 each represents a methine group such as



$C=(amide)-$, etc.; n represents an integer of from 1 to 3; R_1 , R_2 , R_3 and R_4 each represents an alkyl group, (preferably an unsubstituted lower alkyl group containing from 1 to 4 carbon atoms), e.g., methyl, ethyl, propyl, isopropyl, butyl, hexyl, cyclohexyl, decyl, dodecyl, etc., an alkenyl group, e.g., allyl, 1-propenyl, 2-butenyl, etc.; or an aryl group, e.g., phenyl, tolyl, naphthyl, methoxyphenyl, chlorophenyl, etc.; and, X represents an acid anion, such as chloride, bromide, iodide, thiocyanate, sulfonate, perchlorate, p-toluenesulfonate, methyl sulfate, ethyl sulfate and so forth. Particularly good results are obtained with the benzimidazolocarbocyanine dyes. Especially useful are the imidazolocarbocyanine dyes having the above formula wherein Z_1 and Z_2 each represents the atoms to complete a 5,6-dichlorobenzimidazole nucleus, and R_1 , R_2 , R_3 and R_4 each represents an alkyl group having from 1 to 4 carbon atoms.

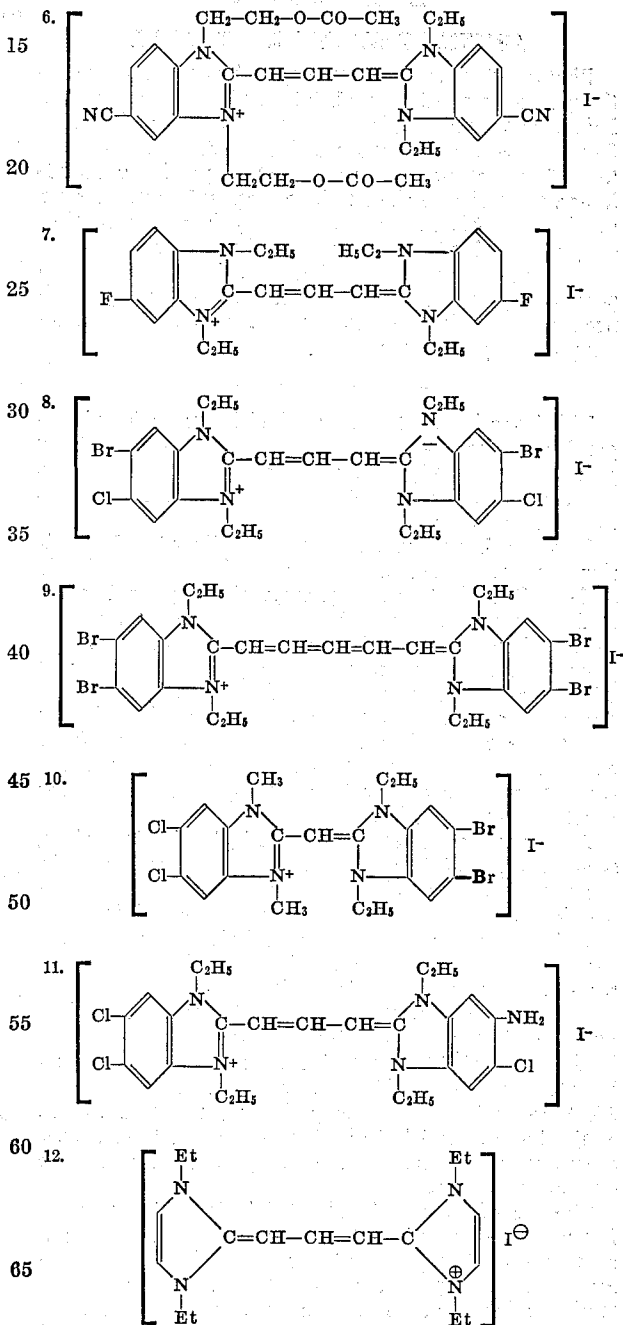
A large number of typical useful cationic imidazolocyanine dyes are described in the following patents: Van Lare U.S. Patent 2,739,149 issued Mar. 20, 1956; Kalenda U.S. Patent 3,173,791 issued Mar. 16, 1965; Belgian Patent 640,453; British Patent 955,964 published Apr. 22, 1964; British Patent 955,962, published Apr. 22, 1964; British Patent 979,251 published Jan. 1, 1965; British Patent 980,234 published Jan. 13, 1965; and British Patent 983,700, published Feb. 17, 1965.

Specific imidazolocyanine dyes which can be used in this practice of this invention include those listed in Table I:

4

TABLE I

- (1) 5,5',6,6'-tetrachloro-1,1',3,3'-tetraethylbenzimidazolocarbocyanine iodide
- (2) 4,4',5,5'-tetrachloro-1,1',3,3'-tetraethylbenzimidazolocarbocyanine iodide
- (3) 5,5'-dichloro-1,1',3,3'-tetraethylbenzimidazolocarbocyanine iodide
- (4) 1,1',3,3'-tetraethyl-5,5'-dichlorobenzimidazolocarbocyanine iodide
- (5) 3,3'-diethyl-1,1'-diphenylbenzimidazolocarbocyanine bromide



In accordance with this invention, photographic silver halide emulsions containing color former are coated on hydrophobic surfaces. As used herein, the term "color formers" includes any of those compounds which react or "couple" with the oxidation product of primary aromatic amino developing agents (e.g., a paraphenylenediamine) on photographic color development to form a dye,

and are non-diffusible in photographic silver halide emulsions. Typical useful color formers include phenolic, 5-pyrazolone, and open chain ketomethylene compounds, such as those described and referred to in U.S. Patents 2,322,027 and 2,801,171. Typical useful couplers producing cyan images which can be used herein are described by Graham et al. U.S. Patent 3,046,129 issued July 24, 1962 at Cols. 15 and 16. Typical couplers producing magenta images which can be used in this invention are described by Graham et al., supra, Col. 11. Couplers typical of those which can be used in this invention to produce yellow images are described by Graham et al., supra, Cols. 17 and 18. Such color formers can be dispersed in any suitable coupler solvent such as one of those described in any of the following U.S. patents: 2,304,939; 2,322,027; 2,801,170; 2,801,171 and 2,949,360.

The photographic silver halide emulsions utilized in the processes hereof are preferably spectrally sensitized first with a dye of the type described herein, and then photographic color former is added to the emulsion. However, the order of addition of spectral sensitizer and then color former to the emulsion is not essential to the practice of this invention.

The present invention is practiced by coating spectrally sensitized photographic silver halide emulsions containing color former onto a hydrophobic surface which has been subjected to corona discharge. The term "hydrophobic" is used herein in its normal sense as inclusive of substances which do not absorb or adsorb water. Typical hydrophobic surfaces which are advantageously electron bombarded include any hydrophobic materials which can be electron bombarded to improve adhesion, such as continuous hydrophobic films (which may or may not be self supporting) that have an ionizable hydrogen or hydroxyl group. Specific supports having hydrophobic surfaces that can be utilized in the practice of this invention include electron bombarded poly(ethylene terephthalate) films, such as those electron bombarded to have a contact angle less than 45°, by the process described in Carroll et al. U.S. Patent 3,20,842, issued Nov. 30, 1965 (which disclosure is incorporated herein by reference); electron bombarded surfaces comprising a chromium halide complex, such as sterato chromic chloride, for example those which are electron bombarded by the process described by Crawford et al. U.S. Patent 3,117,865, issued Jan. 14, 1964 (which disclosure is incorporated herein by reference); and, electron bombarded hardened gelatin coatings, such as hardened gelatin coated papers, e.g., by the process described by Crawford and Venor U.S. patent application Ser. No. 411,059 filed Nov. 13, 1964 and corresponding Belgian Patent 671,661, Nov. 15, 1965 (which disclosure is incorporated herein by reference). Other hydrophobic surfaces which can be electron bombarded for use in the present invention, using processes and apparatus similar to that described in the literature referred to herein, include poly-olefins, preferably derived from olefins having from 2 to 10 carbon atoms; polyamides; polyacetals, polycarbonates; and, cellulose esters and ethers such as cellulose triacetate, cellulose acetate butyrate, ethyl cellulose, etc.

The preferred hydrophobic surfaces utilized in the practice of this invention are polyolefins, polyethylene and polypropylene being especially useful. The support can be composed exclusively of polyolefin. That is, self supporting polyolefin films can be electron bombarded and coated substantially immediately after electron bombardment with spectrally sensitized photographic silver halide emulsions containing color former, in accordance with this invention. The invention can also be practiced when the polyolefin surface is a permanent support for the photographic emulsion, the polyolefin support being removably adhered to a suitable temporary support to form a stripping film of the type described by Goffe et al. U.S. Patent 3,359,107, issued Dec. 19, 1967. Other polyolefin coated supports can also be utilized, such as polyethylene or polypropylene coated paper supports.

The polyolefin surface can be electron bombarded by any convenient method, such as that by Alsup and Venor in British Patents 971,058, and 1,060,526. As noted in those patents, any suitable corona discharge or electron bombardment apparatus can be employed, such as the apparatus disclosed in U.S. Patents 2,864,755 and 2,864,756. When the surface is polyethylene, it is desirable to subject the polyolefin surface to sufficient corona discharge or electron bombardment to obtain a contact angle of less than about 75°. A contact angle of less than about 54° is desirable when the polyolefin utilized is polypropylene. The method for obtaining and determining the contact angle of the corona discharge treated surface is described by Alsup and Venor in British Patent 971,058 and by TAPPI (Technical Association of the Pulp and Paper Industry) specification T458M-59.

When a paper support is used and a hydrophobic film is coated thereover, it is advantageous to incorporate an anti-static agent in just the paper, as described in Chu et al. U.S. Patent 3,253,922, issued May 31, 1966.

This invention is practiced by coating spectrally sensitized emulsion containing color former onto a hydrophobic surface substantially immediately after the hydrophobic surface has been subjected to corona discharge treatment. As used herein and in the appended claims, "substantially immediately" after corona discharge treatment refers to a period within about 30 minutes, and is advantageously within a few seconds (from less than one second up to about 30 seconds) after the corona discharge treatment. In the preferred mode of carrying out this invention, a web having a hydrophobic surface is continuously passed by a first station where the hydrophobic surface is electron bombarded, and then to a second station where a spectrally sensitized emulsion containing color-former is coated onto the electron bombarded hydrophobic surface. Utilizing such techniques, the interval between electron bombardment and coating the emulsion is generally less than a few seconds, and can be a fraction of a second, depending upon the speed selected for operation.

This invention may be satisfactorily utilized when a spectrally sensitized emulsion containing color former is coated as a single layer upon a support of the type described herein, or when a plurality of emulsion coatings are applied to such support. When a plurality of coatings are applied to the support, suitable multiple coating techniques of the type heretofore utilized in photographic processes can be employed. When multiple emulsion coatings are applied over a corona discharge treated hydrophobic surface, the most serious problems of mottle appear in the two emulsion layers closest the hydrophobic surface. The problem of mottle has generally not been too severe with emulsions coated further from the support than two emulsion layers.

The present invention is especially well suited to the preparation of multicolor photographic elements having light sensitive layers of the general type described in Knott et al. Belgian Patent 641,414, issued Jan. 16, 1964, and corresponding U.S. patent application Ser. No. 373,020 filed June 5, 1964. Thus, a support having a hydrophobic surface, such as a polyethylene or polypropylene coated paper support, can have coated thereon, in the following order, a blue sensitive photographic silver halide emulsion layer containing a yellow coupler, an optional inter-layer comprising a hydrophilic colloid such as gelatin; a green sensitive photographic silver halide emulsion layer containing a magenta coupler; an optional hydrophilic colloid layer such as gelatin; and, a red sensitive photographic silver halide emulsion layer containing a cyan coupler. When such photographic silver halide emulsions are coated on an electron bombarded hydrophobic surface, mottle is most severe in the magenta dye image produced by green sensitive silver halide emulsion layer. When the blue sensitive layer contains a spectral sensitizer other than one of the type described herein, mottle

is severe in the yellow dye image. In the arrangement just described, the cyan dye image formed by the red sensitive layer does not appear to be seriously susceptible to mottle. When a similar multicolor element is desired but the red sensitive emulsion layer is coated adjacent the polyolefin surface, with the green and blue sensitive emulsion layers thereover, the most serious mottle appears in the cyan and magenta dye images produced by the spectrally sensitized red and green sensitive emulsions.

The term "mottle" as used herein as a word of art which describes a defect occurring when a light sensitive silver halide emulsion layer containing color former is subjected to an overall even exposure, color developed to provide a dye image, and the dye image, which should have even dye density throughout, instead exhibits "finger" or "lightning" marks which are areas having distinctly higher dye density than that of the remaining areas of the dye image. The areas having the higher dye density exhibit greater density than would be expected or predicted from the photographic speed of the particular system. Mottle is also frequently accompanied by a lower speed than would be predicted in areas outside the "finger" or "lightning" marks. Frequently, the speed loss is about .1 Log *E* over that which would be predicted from the results obtained with a mottle free element corresponding to the test element.

The following examples are included for a further understanding of the invention. The dye numbers given in these examples correspond to dyes of the same number listed in Table I above.

Example 1

A photographic silver bromoiodide emulsion is spectrally sensitized with 142 mg. per mole of silver of dye 1, [5,5',6,6' - tetrachloro - 1,1',3,3' - tetraethyl-benzimidazolocarboyanine iodide]. A coupler is added to form a magenta image, the coupler being a pyrazolone coupler of the type described in Loria et al. U.S. Patent 2,600,788, dated June 17, 1952 (e.g., 3-{3'-[2'',4''-ditert amyphenoxy]acetamido]benzamido} - 1 - (2',4',6'-trichlorophenyl)-5-pyrazolone), dissolved in a suitable coupler solvent, such as dibutyl phthalate. A polyethylene coated paper support is electron bombarded with a corona discharge by the process described in Alsup and Venor British Patent 971,058, the polyethylene surface passing the corona discharge station at the rate of about 500 feet per minute. The polyethylene has a contact angle of less than 76°. At a station situated just beyond the corona discharge apparatus, the spectrally sensitized silver chlorobromide gelatin emulsion containing magenta coupler is coated onto the support, at a concentration of about 95 mg. silver per square foot, about 165 mg. gelatin per square foot and about 65 mg. coupler per square foot. The emulsion passes the coater at the same rate it is passing by the corona discharge apparatus. The coated sample is chill set, dried and processed exactly as described in Col. 5, line 40 through Col. 6, line 44 of Van Campen U.S. Patent 2,956,879. The coating is then exposed to green radiation, i.e., radiation of about 500-600 nm. The dye image is free from mottle. Similar results are obtained when the polyethylene coated support is replaced with polypropylene coated paper, the polypropylene being electron bombarded to provide a contact angle of less than about 54° as described by Alsup and Venor in British Patent 1,060,526; or by a hardened gelatin coated paper electron bombarded as described by Crawford and Venor in Belgian Patent 671,661; or sterato chromic chloride coated paper electron bombarded as described by Crawford and Venor in U.S. Patent 3,117,865; or, poly(ethylene)terephthalate electron bombarded as described by Carroll and Chapman in U.S. Patent 3,220,842. The speed of the emulsion coating of Example 1 is the same as the speed of a control coating prepared in exactly the same way except that the emulsion is coated two hours after the paper is electron bombarded.

Example 2

Results generally similar to those of Example 1 are obtained when dye 1 is replaced with an equivalent quantity of dye 2.

Example 3

Results generally similar to those of Example 1 are obtained when dye 1 is replaced with an equivalent quantity of dye 3.

Example 4

Results generally similar to those of Example 1 are obtained when dye 1 is replaced with an equivalent quantity of dye 4.

Example 5

Results generally similar to those of Example 1 are obtained when dye 1 is replaced with an equivalent quantity of dye 5.

Example 6

Results generally similar to those of Example 1 are obtained when dye 1 is replaced with an equivalent quantity of dye 6.

Example 7

Results generally similar to those of Example 1 are obtained when dye 1 is replaced with an equivalent quantity of dye 7.

Example 8

Results generally similar to those of Example 1 are obtained when dye 1 is replaced with an equivalent quantity of dye 8.

Example 9

Results generally similar to those of Example 1 are obtained when dye 1 is replaced with an equivalent quantity of dye 9.

Example 10

Results generally similar to those of Example 1 are obtained when dye 1 is replaced with an equivalent quantity of dye 10.

Example 11

Results generally similar to those of Example 1 are obtained when dye 1 is replaced with an equivalent quantity of dye 11.

Example 12

Results generally similar to those of Example 1 are obtained when dye 1 is replaced with an equivalent quantity of dye 12.

Examples 13-24

The procedure of Examples 1-12 are repeated except that the dispersion of pyrazolone coupler is replaced with about 50 mg. per square foot of a cyan forming coupler, e.g., coupler number 1 of Fierke et al. U.S. Pat. 2,801,171 (col. 2) in a conventional coupler solvent such as tri-o-cresyl phosphate. The emulsion is coated at about 65 mg. silver per square foot, 50 mg. cyan coupler per square foot and 110 mg. gelatin per square foot. The results obtained in Examples 13-24 are essentially the same as those of Examples 1-12; i.e., the cyan dye images are free from mottle. Similar results are obtained when the polyethylene coated support is replaced with polypropylene coated paper, the polypropylene being electron bombarded to provide a contact angle of less than about 54° as described by Alsup and Venor in British Pat. 1,060,526; or by a hardened gelatin coated paper electron bombarded as described by Crawford and Venor in Belgian Pat. 671,661; or sterato chromic chloride coated paper electron bombarded as described by Crawford and Venor in U.S. Pat. 3,117,865; or, poly(ethylene)terephthalate electron bombarded as described by Carroll and Chapman in U.S. Pat. 3,220,842.

9
Examples 25-36

The procedure of Examples 1-12 is repeated except that the pyrazolone coupler dispersion is replaced with a yellow image dye-forming coupler, e.g., coupler No. 1 of McCrossen et al. U.S. Pat. 2,875,057, issued Feb. 24, 1959, dispersed in dibutyl phthalate, and the emulsion is coated at about 70 mg. per square foot silver, 115 mg. per square foot gelatin and 50 mg. per square foot coupler. The yellow dye images obtained are free from mottle. Similar results are obtained when the polyethylene coated support is replaced with polypropylene coated paper, the polypropylene being electron bombarded to provide a contact angle of less than about 54° as described by Alsup and Venor in British Pat. 1,060,526; or by a hardened gelatin coated paper electron bombarded as described by Crawford and Venor in Belgian Pat. 671,661; or sterato chromic chloride coated paper electron bombarded as described by Crawford and Venor in U.S. Pat. 3,117,865; or, poly(ethylene) terephthalate electron bombarded as described by Carroll and Chapman in U.S. Pat. 3,220,842.

Example 37

A polyethylene coated paper support is electron bombarded to provide a contact angle of less than 75° on the polyethylene surface. Substantially immediately after the electron bombardment, i.e., within seconds after the electron bombardment, blue, green and red sensitive silver halide emulsion layers containing, respectively, yellow, magenta, and cyan color formers are simultaneously coated, from a multiple coating hopper, onto the electron bombarded polyolefin surface, the blue sensitive layer containing yellow color former being closest to the electron bombarded polyethylene surface with the green sensitive layer containing magenta coupler over the blue sensitive layer and the red sensitive layer containing cyan color former overlying the green sensitive layer and being furthest from the polyethylene surface. The blue sensitive layer does not contain a spectral sensitizing dye. The yellow image forming coupler is coupler No. 1 of McCrossen et al. U.S. Pat. 2,875,057, issued Feb. 24, 1959, dispersed in dibutyl phthalate and coated at a concentration of 115 mg. per square foot gelatin, 70 mg. per square foot silver and 50 mg. per square foot coupler. The green sensitive silver halide emulsion layer is spectrally sensitized with 149 mg. per mole of silver with dye 1, 5,5',6,6'-tetrachloro-1,1',3,3'-tetraethyl-benzimidazolocarbo-cyanine iodide. The green sensitive emulsion layer has dispersed therein pyrazole coupler No. 7 of Fierke et al. U.S. Pat. 2,801,171, (col. 2) dissolved in coupler solvent, such as tri-*o*-cresyl phosphate. The green sensitive layer is coated at the rate of 165 mg. per square foot gelatin, 95 mg. per square foot silver and 65 mg. per square foot coupler. The red sensitive layer is spectrally sensitized with a conventional sensitizer, such as anhydro-3,3'-di(β -sulfoethyl)thiadicarbocyanine hydroxide at a concentration of about 130 mg. sensitizing dye per mole of silver. The red sensitive layer contains a dispersion of coupler No. 1 of Fierke et al. U.S. Pat. 2,801,171 (col. 2) in a coupler solvent, such as tri-*o*-cresyl phosphate. The red sensitive emulsion layer is coated at the rate of 110 mg. per square foot gelatin, 65 mg. per square foot silver, 50 mg. per square foot cyan coupler.

The element is given a color sensitometric exposure and processed as described in Van Campen U.S. Patent 2,956,879, Col. 5, line 40 through Col. 6, line 44. The yellow, magenta and cyan dye images obtained are free from mottle. No speed loss is observed when the speed of each of the emulsion layers is compared to an element having the same emulsion layers but coated on a baryta coated paper which is not electron bombarded. Similar results are obtained when the polyethylene coated support is replaced with polypropylene coated paper, the polypropylene being electron bombarded to provide a con-

10

tact angle of less than about 54° as described by Alsup and Venor in British Patent 1,060,526; or by a hardened gelatin coated paper electron bombarded as described by Crawford and Venor in Belgian Patent 671,661; or sterato chromic chloride coated paper electron bombarded as described by Crawford and Venor in U.S. Patent 3,117,865; or, poly(ethylene) terephthalate electron bombarded as described by Carroll and Chapman in U.S. Patent 3,220,842.

The above examples show that mottle-free images can be obtained with emulsions spectrally sensitized with cationic imidazolocyanine dyes, even when such emulsions are coated on electron bombarded hydrophobic supports substantially immediately after the electron bombardment treatment. The examples also show that the speed of emulsions containing the cationic imidazolocyanine dyes have essentially the same speed as control emulsions prepared in exactly the same manner except that a two hour holding period is utilized between the electron bombardment treatment and coating of the spectrally sensitized emulsions. These results are particularly surprising since closely related dyes either result in mottled images, or in undesirable speed loss. The results obtained with such closely related dyes are shown in the following examples.

Example 38

The procedure of Example 1 is repeated except that dye 1 is replaced with 130 mg. per mole of silver of 3,3',9-triethyl-5,5' - diphenyloxacarbocyanine bromide. Severe mottle is readily apparent in the magenta dye image.

Example 39

The procedure of Example 1 is repeated except that dye 1 is replaced with 130 mg. per mole of silver of 9-ethyl - 3,3' - di(β -methoxyethyl)-5,5'-diphenyloxacarbocyanine iodide. Severe mottle is readily apparent in the magenta dye image.

Example 40

The procedure of Example 1 is repeated except that dye 1 is replaced with 130 mg. per mole of silver of anhydro-3,3' - di(β -carboxyethyl)-9-ethyl-5,5'-diphenyloxacarbocyanine hydroxide. Severe mottle is readily apparent in the magenta dye image.

Example 41

The procedure of Example 1 is repeated except that the emulsion is spectrally sensitized with 126 mg. per mole of silver of anhydro-1,1'-di(β -carboxyethyl)-5,5',6,6'-tetrachloro-3,3'-diethyl-benzimidazolocarbo-cyanine hydroxide. Although no mottle is observed, the emulsion exhibits a speed loss of .02 log *E* when compared to a control prepared in exactly the same way except that the two hour holding period was utilized between electron bombardment of the support and coating of the emulsion thereon.

Example 42

The procedure of Example 1 is repeated except that the emulsion is spectrally sensitized with 156 mg. per mole of silver of anhydro-5,5',6,6'-tetrachloro-1,1'-diethyl-3,3' - di(3 - sulfobutyl)benzimidazolocarbo-cyanine hydroxide. Although no mottle is observed, the emulsion exhibits a speed loss of .04 log *E* when compared to a control prepared in exactly the same way except that the two hour holding period was utilized between electron bombardment of the support and coating of the emulsion thereon.

Example 43

The procedure of Example 1 is repeated except that the emulsion is spectrally sensitized with 137 mg. per mole of silver of anhydro-5,5',6,6'-tetrachloro-1,1',3-triethyl - 3'-(3-sulfobutyl)-benzimidazolocarbo-cyanine hydroxide. Although no mottle is observed, the emulsion exhibits a speed loss of .08 log *E* when compared to a con-

trol prepared in exactly the same way except that the two hour holding period was utilized between electron bombardment of the support and coating of the emulsion thereon.

In the preparation of the above photographic elements by the process of this invention, the sensitizing dyes can be incorporated in the washed, finished silver halide emulsion and should, of course, be uniformly distributed throughout the emulsion. The methods of incorporating dyes and other addenda in emulsions are relatively simple and well known to those skilled in the art of emulsion making. For example, it is convenient to add them from solutions in appropriate solvents, in which case the solvent selected should be completely free from any deleterious effect on the ultimate light-sensitive materials. Methanol, isopropanol, pyridine, water, etc., alone or in admixtures, have proven satisfactory as solvents for this purpose. The type of silver halide emulsions that can be sensitized in the process of this invention include any of those prepared with hydrophilic colloids that are known to be satisfactory for dispersing silver halides, for example, emulsions comprising natural materials such as gelatin, albumin, agar-agar, gum arabic, alginic acid, etc. and hydrophilic synthetic resins such as polyvinyl alcohol, polyvinyl pyrrolidone, cellulose ethers partially hydrolyzed cellulose acetate, and the like. Any suitable silver halide can be used, such as silver chloride, silver bromide, silver bromoiodide, silver chlorobromide, etc.

The binding agents for the emulsion layer of the photographic element can also contain dispersed polymerized vinyl compounds. Such compounds are disclosed, for example, in U.S. Patents 3,142,568; 3,193,386; 3,062,674 and 3,220,844 and include the water insoluble polymers of alkyl acrylates and methacrylates, acrylic acid, sulfoalkyl acrylates or methacrylates and the like.

The cationic imidazolocyanine dyes can be used in any suitable concentration in the practice of this invention. Good results are obtained, for example, with from about 50 to 200 mg. dye per mole of silver. However, optimum concentrations vary widely, depending on the particular dye and emulsion used.

The problem of dye mottle which occurs when emulsions containing color former are coated on corona discharge treated hydrophobic supports does not occur when a long holding period is initiated between the corona discharge treatment of the support and coating of the emulsion onto the support. Thus, when the examples hereof are repeated, with at least a two hour holding period between the corona discharge treatment of the polyolefin surface and the coating of the emulsion, no mottle is apparent.

The cause of mottle in dye images produced when conventional methine dyes are used to sensitize silver halide emulsions containing color former, when the emulsions are coated on a hydrophobic surface substantially immediately after it has been electron bombarded, is not fully understood. It may be related to ozone or nascent oxygen, which is present on electron bombarded hydrophobic surfaces substantially immediately after electron bombardment. The reason why sulfo-substituted methine dyes avoids mottle, whether caused by nascent oxygen, ozone or some other cause, is not known.

The invention has been described in detail with particular reference to preferred embodiments thereof, but, it will be understood that variations and modifications can be effected within the spirit and scope of the invention described hereinabove and in the appended claims.

We claim:

1. The method for preparing a light sensitive photographic element which provides dye images substantially free from mottle which comprises:

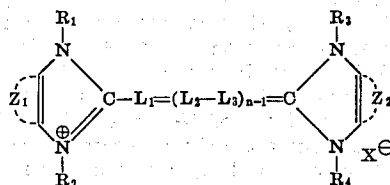
- (1) spectrally sensitizing a light sensitive photographic silver halide emulsion with a cationic imidazolocyanine dye;
- (2) incorporating photographic color coupler in said emulsion;

(3) electron bombarding a hydrophobic surface to provide good adhesion for said emulsion; and,

(4) coating said emulsion onto said hydrophobic surface within about 30 minutes after said electron bombarding treatment.

2. The method for preparing a light sensitive photographic element as defined in claim 1 wherein said cyanine dye is a benzimidazolocarbocyanine dye.

3. The method for preparing a light sensitive photographic element as defined in claim 1 wherein said cationic imidazolocyanine dye has the following general formula:



wherein Z_1 and Z_2 each represent the atoms necessary to complete an aryl group; L_1 , L_2 and L_3 each represents a methine linkage; n represents an integer of from 1 to 3; R_1 , R_2 , R_3 and R_4 each represents a member selected from the class consisting of an alkyl group, an alkenyl group and an aryl group; and, X represents an acid anion.

4. The method for preparing a light sensitive photographic element as defined in claim 3 wherein said Z_1 and said Z_2 each represents the atoms necessary to complete a benzo group.

5. The method for preparing a light sensitive photographic element as defined in claim 4 wherein said dye is a symmetrical benzimidazolocarbocyanine dye.

6. The method for preparing a light sensitive photographic element as defined in claim 1 wherein said color coupler is selected from the group consisting of phenolic, 5-pyrazolone, and open chain ketomethylene photographic couplers, said couplers being dissolved in a solvent and the solution being dispersed in the photographic silver halide emulsion.

7. The method for preparing a light sensitive photographic element as defined in claim 1 wherein said hydrophobic surface is selected from the group consisting of a poly- α -olefin, a polyester, a polyamide, a polyacetal, a polycarbonate, a cellulose ester, a cellulose ether and hardened gelatin.

8. The method for preparing a light sensitive photographic element as defined in claim 3 wherein said hydrophobic surface is selected from the group consisting of a poly- α -olefin, a polyester, a polyamide, a polyacetal, a polycarbonate, a cellulose ester, a cellulose ether and hardened gelatin.

9. The method for preparing a light sensitive photographic element which comprises:

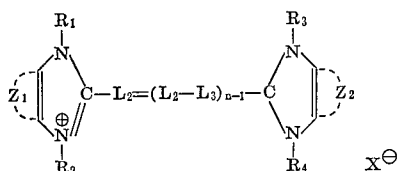
- (1) spectrally sensitizing a photographic silver bromoiodide emulsion with the dye 5,5',6,6'-tetrachloro-1,1',3,3' - tetraethyl-benzimidazolocarbocyanine iodide;
- (2) dispersing in the said silver halide emulsion a solution of photographic pyrazolone color coupler dissolved in a solvent;
- (3) electron bombarding the polyethylene surface of a polyethylene coated paper support, said electron bombardment being of sufficient intensity to provide a contact angle on the polyethylene surface of less than 76° ;
- (4) coating said spectrally sensitized silver halide emulsion containing pyrazolone coupler onto said electron bombarded polyethylene surface within about one minute from the time of said electron bombardment.

10. A photographic element which provides dye images substantially free from mottle comprising a support which has an electron bombarded hydrophobic surface and, a photographic silver halide emulsion coating thereover spectrally sensitized with an imidazolocarbo-

13

cyanine dye, and containing photographic color coupler.

11. A photographic element as defined in claim 10 wherein said methine dye has the following formula:



wherein Z and Z₂ each represents the atoms necessary to complete an aryl group; L₁, L₂ and L₃ each represents a methine linkage; n represents an integer of from 1 to 3; R₁, R₂, R₃ and R₄ each represent a member selected from the class consisting of an alkyl group, an alkenyl group and an aryl group; and, X represents an acid anion.

12. A photographic element as defined in claim 11 wherein said Z₁ and said Z₂ each represents the atoms necessary to complete a benzo group.

13. A photographic element prepared by the method defined in claim 1.

14. A photographic element prepared by the method defined in claim 3.

14

15. A photographic element prepared by the method defined in claim 9.

16. A photographic element which provides dye images substantially free from mottle comprising a support having a polyethylene surface electron bombarded to provide a contact angle of less than 76°, said polyethylene surface having coated thereover a photographic silver halide emulsion spectrally sensitized with 5,5',6,6'-tetrachloro - 1,1',3,3' - tetraethylbenzimidazolocarbocyanine iodide, and containing the photographic color coupler 3 - {3' - [2'',4'' - di - tert amylphenoxy]acetamido} - benzamido} - 1 - (2',4',6' - trichlorophenyl) - 5 - pyrazolone.

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25 117—34