United States Patent

[11] **3,632,348**

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[54] METHINE DYE SENSITIZERS FOR EMULSIONS EXPOSED AT−180° C.

6 Claims, 3 Drawing Figs.

[52] **U.S. Cl.** **96/107,**
69/129, 96/130, 96/131, 96/134
[51] **Int. Cl.** **G03c 1/28,**
G03c 1/08, G03c 1/10
[50] **Field of Search** 96/107,
129, 130, 131, 134

[56] **References Cited**

OTHER REFERENCES

West, " Temperature-Dependence of Spectral Sensitization by Dye Series of Regularly Increased Chain Length and the Mechanism of Spectral Sensitization" In PS&E, Vol. 6 (1962) page 92- 101

Mees & James, " The Theory of the Photographic Process," cRD Ed. (the MacMillan Co., 1966) pages 19- 21, 264 & 265

Toni et al., " Cal. of Electronic Energy Levels of Photo Sensitizing Dyes" PS&E, Vol. 11, No. 3, (1967) pages 129- 144

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ABSTRACT: Photographic silver halide emulsions which are exposed at low temperatures have adsorbed thereto a sufficient amount of a methine dye to increase the sensitivity and contrast of the emulsion at temperatures below about −180° C. The highest occupied electronic energy level of the methine dye adsorbed on the silver halide is more positive than the highest occupied energy level in the valence band of the silver halide, and the lowest vacant electronic energy level of the dye adsorbed on the silver halide is more positive than the conduction band of the silver halide. Particularly good results are obtained with the quinoline monomethine cyanines. Preferred results are obtained when the dye is employed in a concentration sufficient to give monomolecular layer coverage of the silver halide grains.

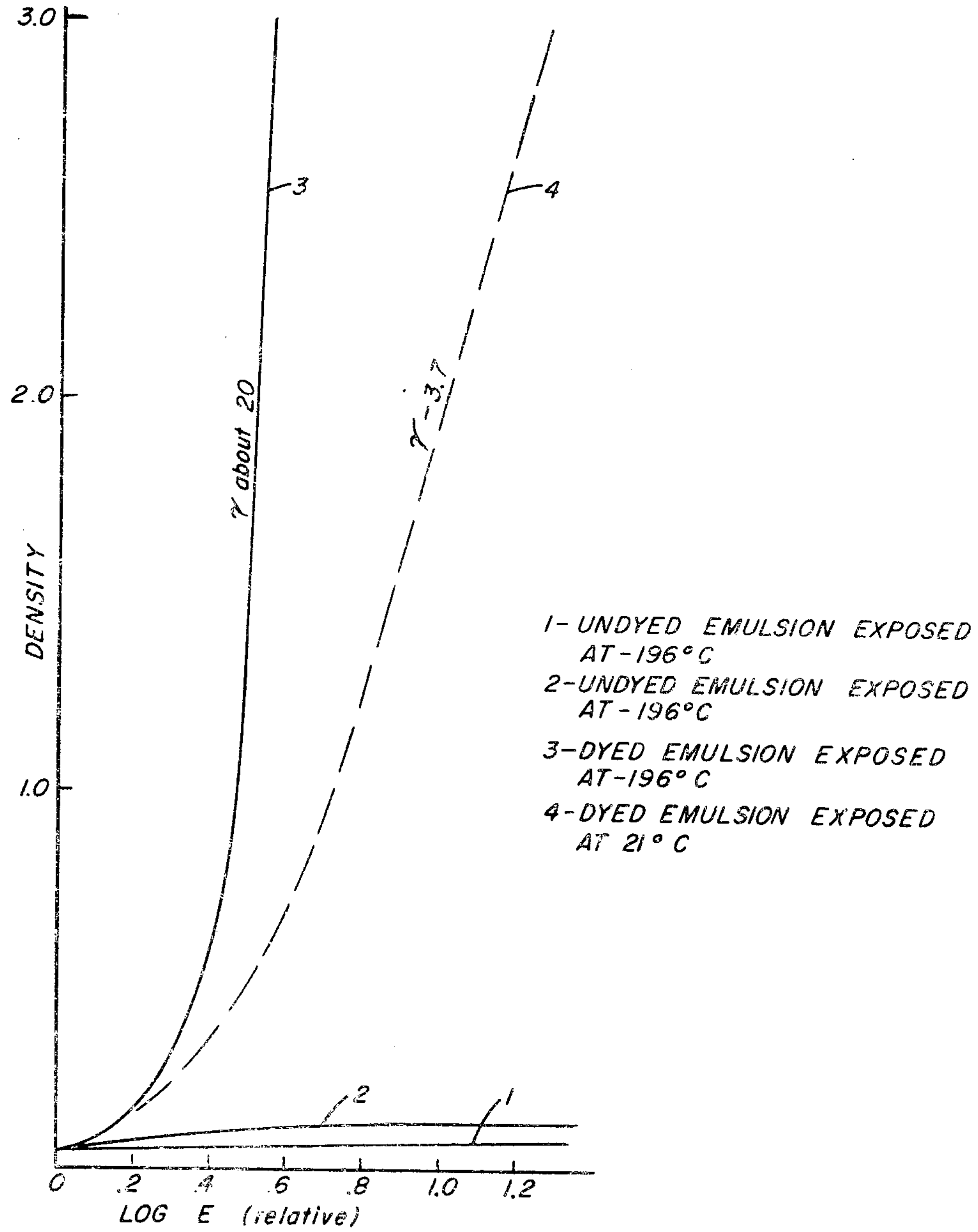

FIG. 1

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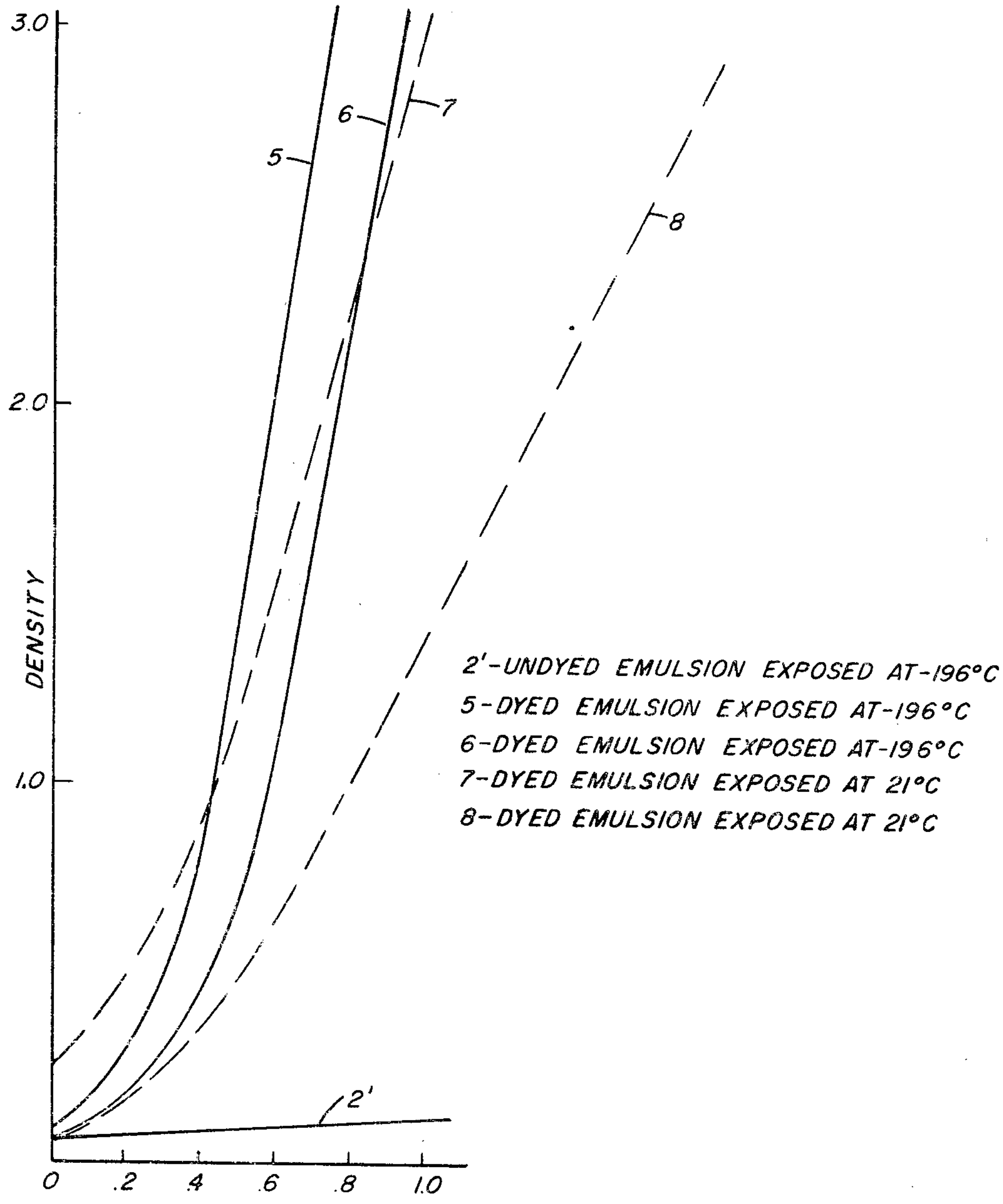

FIG. 2

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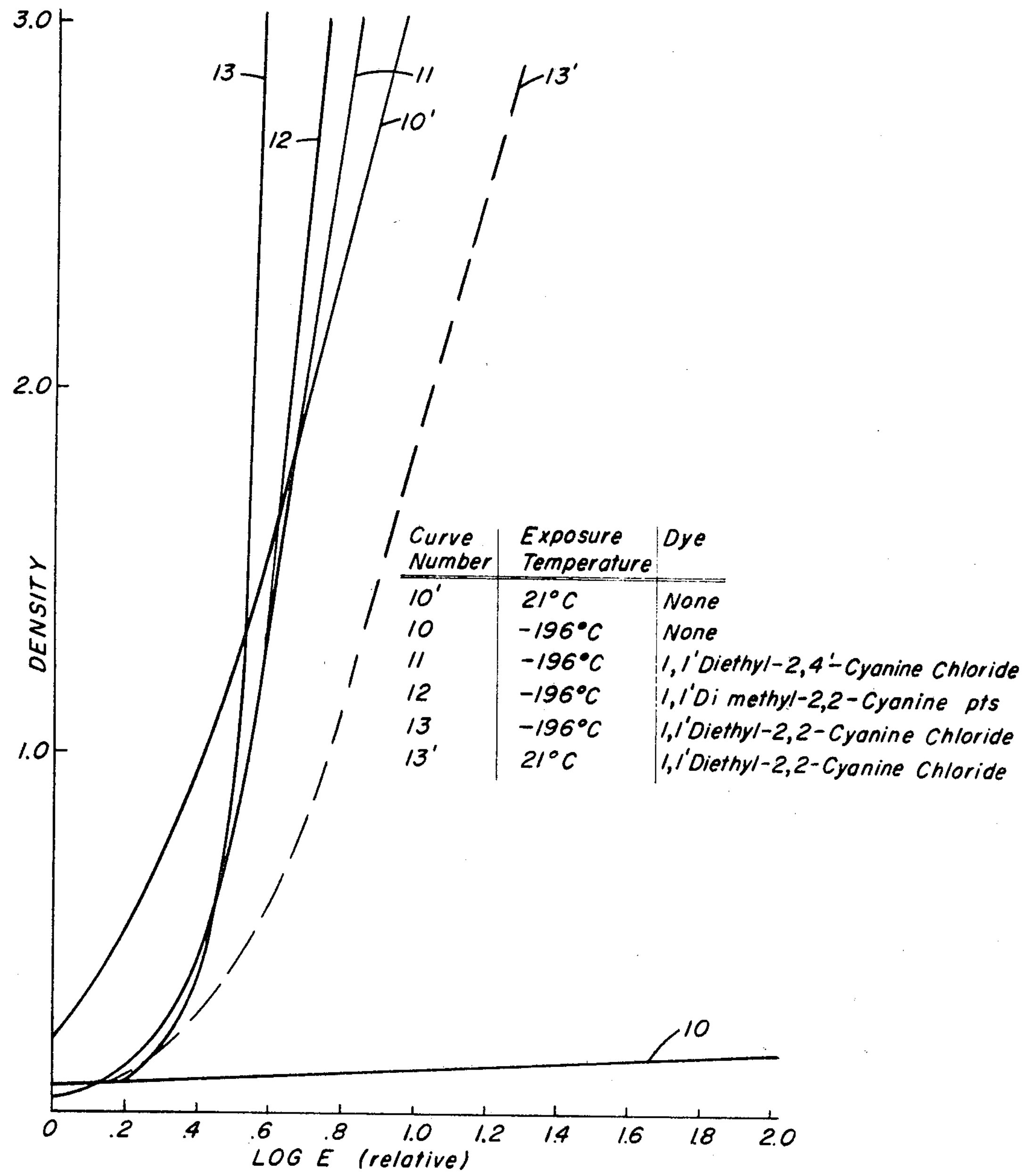

Curve Number	Exposure Temperature	Dye
10'	21°C	None
10	-196°C	None
11	-196°C	1,1'Diethyl-2,4'-Cyanine Chloride
12	-196°C	1,1'Di methyl-2,2-Cyanine pts
13	-196°C	1,1'Diethyl-2,2-Cyanine Chloride
13'	21°C	1,1'Diethyl-2,2-Cyanine Chloride

FIG. 3

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METHINE DYE SENSITIZERS FOR EMULSIONS EXPOSED AT−180° C.

This invention relates to photographic processes, and more particularly to photographic processes in which silver halide emulsions are exposed at low temperatures.

West in *Photographic Science and Engineering*, Volume 6, No. 2, page 92 (1962) at page 95 observes that the absorption of visible light by silver halide decreases with decreasing temperature, and thus a corresponding decrease in sensitivity occurs in the region in which the silver halide absorbs. The presence of spectral sensitizing dyes in the emulsions tends to further decrease the sensitivity of the silver halide at low-temperature exposures, as shown by West. No disclosure is known in the art for effectively increasing the sensitivity of photographic silver halide emulsions for low-temperature exposures.

One object of this invention is to provide a photographic process in which a silver halide emulsion is exposed at low temperatures.

Another object of this invention is to provide a photographic process which results in improved sensitivity of photographic silver halide emulsions when exposed at low temperatures.

Still another object of this invention is to provide photographic processes which result in images of increased contrast when silver halide emulsions are exposed at low temperatures.

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

In accordance with the present invention, an improvement is provided in the process for making photographic images by exposing a light-sensitive photographic silver halide emulsion to radiation at temperatures below about −180° C. to produce a latent image, and then developing the latent image to a silver image. The improvement in accordance with this invention which comprises employing in the process a negative, unfogged, photographic silver halide emulsion having a methine dye adsorbed thereto, the highest occupied electronic energy level of the dye adsorbed on the silver halide being more positive than the highest occupied energy level in the valence band of the silver halide, and the lowest vacant electronic energy level of the dye adsorbed on the silver halide being more positive than the conduction band of the silver halide. The quantity of dye used is sufficient to increase the sensitivity and the contrast of the emulsion when it is exposed at low temperatures. The concentration of the dyes employed in the practice of the invention is generally much higher than amounts of dye used to sensitize photographic silver halide emulsions for normal temperature exposures.

The practice of the present invention results in substantial increases in speed on low-temperature exposure. In addition, very high contrast can be obtained in the practice of the present invention; the contrast can be similar to that obtained with lith-type emulsions used with lith-type developers. The results are particularly unexpected since methine dyes generally decrease low-temperature sensitivity, as shown by West, *Photographic Science and Engineering*, Volume 6, No. 2, page 92 (1962) at page 100.

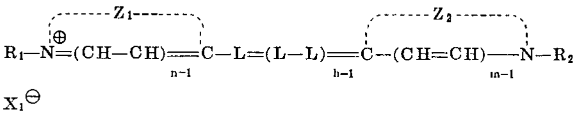
The drawings illustrate the characteristic curve of photographic images made at low-temperature exposures in accordance with the invention, and show comparative characteristic curves for exposures made at room temperature, and at low temperatures but not employing the process of the invention. In each figure, density is plotted on the ordinate and relative log exposure is plotted on the abscissa. Curve **3** of FIG. **1**, curves **5** and **6** of FIG. **2** and curves **11**, **12** and **13** of FIG. **3** show the high sensitivity and contrast obtained at low-temperature exposures in accordance with the process of invention. The curves for corresponding room temperature exposures are shown in FIG. **1** curve **4**, FIG. **2** curves **7** and **8**, and FIG. **3** curve **13′**. Characteristic curves for emulsions containing no dye, at either room-temperature or low-temperature exposures, are shown in curves **1** and **2** of FIG. **1**, curve **2′** of FIG. **2** and curves **10** and **10′** in FIG. **3**. These curves will be further explained in the examples given below.

Any methine dye can be used in the practice of the invention, provided the highest occupied electronic energy level of the dye adsorbed on the silver halide is more positive than the highest occupied energy level in the valence band of the silver halide, and the lowest vacant electronic energy level of the dye adsorbed on the silver halide is more positive than the conduction band of the silver halide. The highest occupied electronic energy level of methine dyes adsorbed on silver halide is preferably more negative than the conduction band of the silver halide. The highest occupied electronic energy level of a methine dye adsorbed on silver halide, and the lowest vacant electronic energy level of a methine dye adsorbed on silver halide, can be calculated by the method described by Tani and Kikuchi, *Photographic Science and Engineering*, Volume 11, No. 3, page 129 (1967) and Tani, Kikuchi, and Honda in *Photographic Science and Engineering*, Vol. 12, No. 2, page 80 (1968).

The highest occupied energy level in the valence band of silver halide and the bottom conduction band of the silver halide has been determined by those skilled in the art. See, for example, Mees, and James, *The Theory of the Photographic Process*, Third Edition, (the MacMillan Company, 1966), pages 19–21, 264 and 265, and Tani, Kikuchi, and Honda, *Photographic Science and Engineering*, Volume 12, No. 2, (1968) page 80. The highest occupied energy level of the valence band of silver halide is about −6.0 ev. relative to 0 for vacuum, and the bottom of the conduction band of silver halide is about −3.5 ev. The values which have been calculated for pure silver bromide result in an energy level in the valance band of approximately −6.0 ev. relative to 0 for vacuum, with the electronic energy of the bottom of the conduction band of the silver bromide being approximately −3.5 ev. Further description of the mechanism for calculating the highest occupied energy level in the valence band and bottom conduction band of silver halides is given in *Grundlagen der photographichen Prozesse mit Silberhalogeniden;* Band 3, 1968, Akademische Verlagsgesellschaft, pages 1,068–1,071.

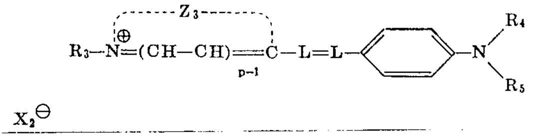
Any of the methine dyes, including the styryl and cyanine methine dyes, can be employed in the practice of the invention, provided the dyes when adsorbed to silver halide, including adsorption in their aggregated state, have a highest occupied electronic energy level and a lowest vacant electronic energy level, respectively, that is more positive than the highest occupied energy level in the valence band of the silver halide and the bottom conduction band of the silver halide. Especially good results are obtained with methine dyes which meet the above criteria and have at least one of the following formulas:

Formula 1



$$R_1-\overset{\oplus}{N}=(CH-CH)_{n-1}=C-L=(L-L)_{h-1}=C-(CH=CH)_{m-1}-N-R_2 \quad X_1^{\ominus}$$

Formula 2



In the above formulas, *h*, *m*, *n* and *p* each represents an integer of from 1 to 2; L represents a methine linkage, e.g., —CH=, —C(CH_3)=, —C(C_6H_5)=, etc.; R_1, R_2 and R_3 each represents an alkyl group, including substituted alkyl, (preferably a lower alkyl containing from one to four carbon atoms), e.g., methyl, ethyl, propyl, isopropyl, butyl, hexyl, cyclohexyl, decyl, dodecyl, etc., and substituted alkyl groups (preferably a substituted lower alkyl containing from one to four carbon atoms), such as a hydroxyalkyl group, e.g., β-hydroxyethyl, ω-hydroxybutyl, etc., an alkoxyalkyl group, e.g., β-methoxyethyl, ω-butoxybutyl, etc., a carboxyalkyl group, e.g., β-carboxyethyl, ω-carboxybutyl, etc., a sulfoalkyl group, e.g., β-sulfoethyl, ω-sulfobutyl, etc., a sulfatoalkyl group, e.g., β-sulfatoethyl, ω-sulfatobutyl, etc., an acyloxyalkyl group, e.g., β-acetoxyethyl, γ-acetoxypropyl, ω-butyryloxybutyl, etc., an alkoxycarbonylalkyl group, e.g., β-methoxycarbonylethyl, ω-ethoxycarbonylbutyl, etc., or an aryl group, e.g., phenyl, tolyl, naphthyl, methoxyphenyl, chlorophenyl, etc.; R_4 and R_5 each represents the same or a different alkyl group containing from one to six carbon atoms, e.g., methyl, ethyl, isopropyl, butyl, 2-cyanoethyl, hexyl, etc.; X_1 and X_2 each represents any acid anion, such as chloride, perchlorate, sulfonate, p-toluene sulfonate and which may be combined in R_1 and R_3 when the dye is a betaine; Z_1, Z_2 and Z_3 each represents the nonmetallic atoms necessary to complete the same or different five- to six-membered heterocyclic nucleus of the type used in methine dyes, which nucleus may contain a second hetero atom such as oxygen, sulfur, selenium or nitrogen, such as the following nuclei: a thiazole nucleus, e.g., thiazole, 4-methylthiazole, 4-phenylthiazole, 5-methylthiazole, 5-phenylthiazole, 4,5-dimethylthiazole, 4,5-diphenylthiazole, 4-(2-thienyl)thiazole, benzothiazole, 4-chlorobenzothiazole, 5-chlorobenzothiazole, 6-chlorobenzothiazole, 7-chlorobenzothiazole, 4-methylbenzothiazole, 5-methylbenzothiazole, 6-methylbenzothiazole, 5-bromobenzothiazole, 6-bromobenzothiazole, 5-phenylbenzothiazole, 5-phenylbenzothiazole, 4-methoxybenzothiazole, 5-methoxybenzothiazole, 6-methoxybenzothiazole, 5-iodobenzothiazole, 6-iodobenzothiazole, 4-ethoxybenzothiazole, 5-ethoxybenzothiazole, tetrahydrobenzothiazole, 5,6-dimethoxybenzothiazole, 5,6-dioxymethylenebenzothiazole, 5-hydroxybenzothiazole, 6-hydroxybenzothiazole, naphtho[2,1-d]thiazole, naphtho[1,2-d]thiazole, 5-methoxynaphtho[2,3-d]thiazole, 5-ethoxynaphtho[2,3-d]thiazole, 8-methoxynaphtho[2,3-d]thiazole, 7methoxynaphtho[d82,3-d]thiazole, 4′-methoxythianaphtheno-7′,6′,-4,5-thiazole, etc., an oxazole nucleus, e.g., 4-methyloxazole, 5-methyloxazole, 4-phenyloxazole, 4,5-diphenyloxazole, 4-ethyloxazole, 4,5-dimethyloxazole, 5-phenyloxazole, benzoxazole, 5-chlorobenzoxazole, 5-methylbenzoxazole, 5-phenylbenzoxazole, 6-methylbenzoxazole, 5,6-dimethylbenzoxazole, 4,6-dimethylbenzoxazole, 5-methoxybenzoxazole, 5-ethoxybenzoxazole, 5-chlorobenzoxazole, 6-methoxybenzoxazole, 5-hydroxybenzoxazole, 6-hydroxybenzoxazole, naphtho[2,1-doxazole, naphtho[1,2-d]-oxazole, etc.; a selenazole nucleus, e.g., 4-methylselenazole, 4-phenylselenazole, benzoselenazole, 5-chlorobenzoselenazole, 5-methoxybenzoselenazole, 5-hydroxybenzoselemazole, tetrahydrobenzoselenazole, naphtho[2,1-d]selenazole, naphtho[1,2-d]selenazole, etc.; and, a quinoline nucleus, e.g., 2-quinoline, 3-methyl-2-quinoline, 5-ethyl-2-quinoline, 6-chloro-2-quinoline, 8-chloro-2-quinoline, 6-methoxy-2-quinoline, 8 -ethoxy-2-quinoline, 8-hydroxy-2-quinoline, 4-quinoline, 6-methoxy-4-quinoline, 7-methyl-4-quinoline, 8-chloro-4-quinoline, 1-isoquinoline, 3,4-dihydro-1-isoquinoline, 3-isoquinoline, etc. Dyes of formula 1 above wherein *h* represents 1 and Z_1 and Z_2 each represents a quinoline nucleus, i.e., quinoline monomethine cyanine dyes, provide particularly good results in the practice of this invention. Some specific dyes which can be used in this invention are listed below:

2-(p-Dimethylaminostyryl)-1-methyl pyridinium salt
1,1′-Diethyl-2,2′-cyanine salt
1,1′-Dimethyl 2,2′-cyanine salt
1,1′-Diethyl-2,4′-cyanine salt
1-Methyl-1′,9-diethyl-2,2′-cyanine salt
1,1′, 3,3′-Tetramethyl-2,2′-cyanine salt
3,3′-Diethylthiacarbocyanine salt
3,3′-Diethyloxacarbocyanine salt
1′,3-Diethylselena-2′-cyanine salt
1,1′-Diphenyl-2,4′-cyanine salt
Anhydro-1′-ethyl-3-β-sulfoethylthia-2′-cyanine hydroxide

The useful concentration of the dyes which can be employed in the practice of this invention will be largely dependent upon the type of dye used, the size and type of the silver halide grains employed, and the particular results desired. Generally good results are obtained with about 0.1 to 1 gram of dye per mole of silver, although higher concentrations can be employed. With some particular dyes, advantageous effects are obtained with as low as about 10 percent of monomolecular layer coverage, with effects increasing with increased dye concentrations up to monomolecular layer coverage. Excess dye over monomolecular layer silver halide coverage can be used, but provides no advantage in the practice of the invention. It is preferred to employ dyes at a concentration which will give monomolecular layer coverage, or nearly monolayer coverage, of the silver halide grains. Typical dye concentrations used to spectrally sensitize photographic emulsions for normal temperature exposures are about 0.02 to 0.08 gram dye per mole of silver. Such concentrations do not effectively increase sensitivity and contrast at temperatures of −180° C. and below. Combinations of dyes can also be used.

The invention can be practiced with any of the light-sensitive photographic silver halides, including silver bromide, silver bromoiodide, silver chloride, silver chlorobromide, and silver chlorobromoiodide. Silver bromoiodide emulsions in which the halide is at least 90 mole percent bromide, are especially useful in the practice of the invention. The silver halide grains can be of any suitable type, such as octahedral or cubic grain. Conventional negative, developing-out, unfogged silver halide emulsions are used in this invention. The silver halide emulsion may contain chemical sensitizers, antifoggants, stabilizers, speed-increasing compounds, hardeners, plasticizers, and may utilize the binders described and referred to in Beavers U.S. Pat. No. 3,039,873 (1962) col. 10–13. Substantial increases in speed and contrast are not observed when direct positive emulsions containing the dyes employed herein are given low-temperature exposures.

The temperatures used in the practice of the invention are from about −180° C. and below, such as down to the temperature of liquid helium, i.e., about −269° C. Liquid air (−186° C.) or liquid nitrogen (−196° C.) can be conveniently used to lower the temperature of silver halide for the low-temperature exposure.

The advantageous effects obtained in the practice of the invention are observed when exposures are conducted at atmospheric pressures or at reduced pressures, such as under high vacuum. The process of the invention is, therefore, adaptable for use in electron microscopes.

Emulsions which have been given low-temperature exposures in accordance with the invention are advantageously processed under conventional conditions, i.e., using standard developers and normal temperatures, such as above about 0° C. for example, up to about 50° C. and preferably at about room temperature or about 20° to 25° C.

The radiation to which the emulsions are exposed while held at a low-temperature can be any radiation to which the emulsions are inherently sensitive, i.e., radiation which the silver halide absorbs, or radiation which is absorbed by the spectral sensitizing dye. Exposures in just the region of absorption by the dye give approximately the same results as do exposures to just radiation to which the silver halide is sensitive.

The following examples are included for a further understanding of the invention.

EXAMPLE 1

A cubic grain emulsion is prepared according to the method described in Illingsworth et al. U.S. Pat. application Ser. No. 500,366 filed Oct. 21, 1965, and corresponding French Pat. No. 1,497,202 by adding an aqueous solution of potassium bromide and potassium iodide and an aqueous solution of silver nitrate in equal molar amounts simultaneously to a rapidly agitated aqueous gelatin solution maintained at a temperature of 70° C. the addition being carried out over a period of 35 minutes. The pH of the aqueous gelatin solution is maintained at 2.0 by occasional additions of sulfuric acid and the pAg is maintained at 9.0 by adjusting the relative rates of addition of the halide and silver nitrate solutions. There is obtained a dispersion of cubic-regular grain silver bromoiodide crystals having an average grain size of about 0.2 microns. About 5 mole percent of the halide of the crystals is iodide. The emulsion is washed and a protective colloid is added in the form of an aqueous gelatin solution. The emulsion is coated on a cellulose acetate base. The coating is exposed for 2 minutes, while immersed in liquid nitrogen (−196° C.), through a step wedge to a 1,000-watt tungsten lamp filtered by a combination of one Wratten 36 filter and one Wratten 38A filter (which filters limit the exposure to the region of inherent sensitivity of the silver halide) and operated at 2,650° K. at a distance of 80 cm. from the film. The exposed film is then developed for 12 min. at 20° C. in a solution of N-methyl-p-aminophenol sulfate 2.5 g., ascorbic acid 10.0 g., sodium metaborate (Kodak Balanced Alkali) 35.0 g., potassium bromide 1.0 g., and water to make 1 liter. It is then fixed, washed and dried. Densities are read on a densitometer through a red filter. The characteristic curve, shown as curve **1** in FIG. **1**, demonstrates the low sensitivity and contrast obtained at the low-temperature exposure. Another strip of the same film is bathed in water for 20 min. at 21° C. dried, then exposed, developed, fixed, washed, and dried as before. The characteristic curve, shown as curve **2** in FIG. **1**, again illustrates the unsatisfactory sensitivity and response of the emulsion when exposed at low temperatures. Another strip of the same film is bathed for 20 min. at 21° C. in a 10^{-4} M aqueous solution of 1,1′-diethyl-2,2′-cyanine p-toluenesulfonate (thus providing approximately monomolecular dye coverage on the silver halide), dried, then one-half of the strip is exposed immersed in liquid nitrogen, developed, fixed, washed, and dried as before. The characteristic curve obtained is shown as curve **3** in FIG. **1**. The second half was exposed in room air at 20° C. under otherwise identical conditions and developed, fixed, washed, and dried as before. The characteristic curve obtained is shown as curve **4** in FIG. **1**. These results clearly demonstrate the remarkable increase in both sensitivity and contrast obtained when emulsions are exposed at low temperatures in accordance with the invention.

EXAMPLE 2

Strips of the film coating described in example 1 are immersed in a 10^{-4} M solution of 1,1′,3,3′-tetramethyl-2,2′-cyanine p-toluenesulfonate or 3,3′-diethylthiacarbocyanine p-toluenesulfonate for 20 min. at 21° C. (providing approximately monomolecular dye layer coverage of the silver halide) and then dried. Half of each strip is exposed at liquid nitrogen temperature and half is exposed in room air at 21° C. The strips are developed, fixed, washed, and dried as in example 1. In FIG. **2**, curve **5** represents the characteristic curve for the part of the strip that had been immersed in the 1,1′,3,3′-tetramethyl-2,2′-cyanine p-toluene sulfonate and exposed at liquid nitrogen temperature (−196° C.) and curve **7** represents the characteristic curve of the part of the strip that had been exposed at room temperature (21° C.). Curve **6** represents the characteristic curve for the part of the strip that had been immersed in the 3,3′-diethylthiacarbocyanine 3,3′solution and exposed at liquid nitrogen temperature and curve **8** represents the characteristic curve of the part of the strip that had been exposed at room temperature. Curve **2′** is the control representing the film that had been bathed in water and exposed at liquid nitrogen temperature (see example 1). It is clear that the dyed film strips show only relatively small differences in threshold sensitivity between exposures at room temperature and at liquid nitrogen temperature. It is further evident that the contrast is higher for exposures at liquid nitrogen temperature than for exposures at room temperature.

EXAMPLE 3

Strips of the film coating described in example 1 are immersed in (strip **11**) 10^{-4} M solution of 1,1′-diethyl-2,4′-cyanine chloride, (strip **12**) 10^{-4} M solution of 1,1′-dimethyl-2,2′-cyanine p-toluene sulfonate, and (strip **13**) 10^{-4} M solution of 1,1′-diethyl-2,2′-cyanine. Approximately monomolecular layer dye coverage is provided on the silver halide grains. The strips are exposed at liquid nitrogen temperature as in example 1, developed, fixed, washed, and dried. Characteristic curves, labeled **11**, **12**, and **13**, are shown in FIG. **3**. The curve labeled **10** represents the undyed, control strip that had been immersed in water only. Curves labeled **10′** and **13′** represent samples of strips **10** and **13** that had been exposed at room temperature rather than liquid nitrogen temperature. It is clear that the dyed film strips show large increases in sensitivity and gamma over the undyed control strip for exposures at the temperature of liquid nitrogen. Moreover, the contrast of the dyed strips is greater for the liquid nitrogen temperature exposure than for a room temperature exposure of either dyed or undyed strips.

EXAMPLE 4

A fine grain, pure silver bromide emulsion is prepared and sulfur-sensitized with sodium thiosulfate. Coatings of this emulsion are immersed for 20 minutes in 10^{-4} M solutions of various dyes, then dried, exposed at liquid nitrogen temperature, developed, fixed, washed, and dried as described in example 1. Table 1 shows the speed and gamma values obtained.

Table 1

Dye	Speed (relative)	Gamma
None	1.1	0.50
2-(p-Dimethylaminostyryl)-1-methyl pyridinium p-toluene sulfonate	2.0	1.35
1,1′-Diethyl-2,2′-cyanine chloride	5.0	6.2
1,1′-Dimethyl-2,2′-cyanine p-toluene sulfonate	6.3	7.0
1,1′-Diethyl-2.4′-cyanine chloride	6.9	7.0
1-Methyl-1′,9-diethyl-2,2′-cyanine perchlorate	11.5	2.2

In the above examples, the highest occupied electronic energy level of each dye adsorbed to the silver halide is more positive than the highest occupied energy level in the valence band of the silver halide, and the lowest vacant electronic energy level of each dye adsorbed in the silver halide is more positive than the conduction band of the silver halide. For example, 1,1′-diethyl-2,2′-cyanine has values of −5.53 ev. and −3.22 ev. for its highest occupied and lowest vacant electronic energy levels, and both of these values are more positive than the valence band (about −6.0 ev. relative to vacuum) and the conduction band (about −3.5 ev.) for silver halide. Phenosafranine has a value of −6.17 ev. for its highest occupied level and −3.84 ev. for its lowest vacant level, which are more negative, respectively, than the valence band and conduction band of silver halide. Phenosafranine does not produce high contrast and sensitivity when emulsions dyed with it are exposed at low (liquid nitrogen) temperatures. Capri blue also fails to sensitize low-temperature exposures. Although the highest occupied level (−5.86 ev.) of Capri blue is more positive than the valence band of silver halide, its lowest vacant level (−4.03 ev.) is more negative than the conduction band of silver halide. Other dyes whose highest occupied or lowest vacant energy level is more negative than, respectively, the valence band or the conduction band of silver halide fail to provide good sensitivity and contrast when adsorbed to silver halide and exposed at low temperatures.

EXAMPLE 5

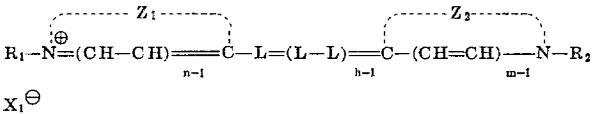
A cubic grain emulsion is prepared as in example 1, except that prior to coating 1,1′-diethyl-2,2′-cyanine chloride in the amount of 0.80 grams per mole of silver is added. This emulsion, when coated, exposed, and developed as in example 1, shows the high contrast and speed for exposure at −196° C. characteristic of the dyed coating described in example 1.

When the dyes employed in the above examples are added to the silver halide emulsion at about 0.02 to 0.08 gram dye per mole of silver, exposure of the emulsion at −196° C. fails to show any effective increase in sensitivity or contrast as compared to control emulsions containing no dye.

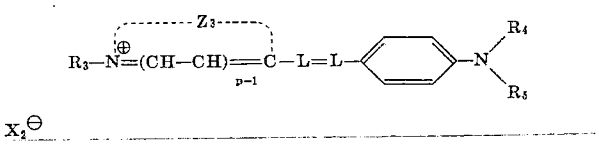
The invention has been described in detail with particular reference to preferred embodiments thereof, but, it will be understood that variations and modifications can be effected within the spirit and scope of the invention.

I claim:

1. In a process of making photographic images wherein a light-sensitive photographic silver halide emulsion is exposed to radiation at a temperature below about −180° C. to produce a latent image, and said latent image is developed to a silver image: the improvement which comprises employing in said process a negative, unfogged photographic silver halide emulsion in which the silver halide grains have adsorbed thereto a methine dye, the highest occupied electronic energy level of said dye being more positive than the highest occupied energy level in the valence band of the silver halide, and the lowest vacant electronic energy level of said dye being more positive than the bottom conduction band of the silver halide, said dye having at least one of the following formulas:



$$R_1-\overset{\oplus}{N}=(CH-CH)_{n-1}=C-L=(L-L)_{h-1}=C-(CH=CH)_{m-1}-N-R_2 \qquad X_1^{\ominus}$$



wherein *h*, *m*, *n* and *p* each represents an integer of from 1 to 2; L represents a methine linkage; R_a, R_2 and R_3 each represents a member selected from the group consisting of an alkyl group and an aryl group; R_4 and R_5 each represents an alkyl group containing from one to six carbon atoms; X_1 and X_2 each represents an acid anion; and, Z_1, Z_2 and Z_3 each represents the atoms necessary to complete a five- to six-membered heterocyclic nucleus of the type used in methine dyes; said silver halide having a sufficient amount of said dye adsorbed thereto to effectively increase the speed of said silver halide when exposed at a temperature below about −180° C.

2. The process of making photographic images as defined in claim 1 wherein said Z_1, Z_2 and Z_3 in the structural formulas each represents the atoms required to complete a nucleus selected from the group consisting of a thiazole nucleus, an oxazole nucleus, selenazole nucleus, and a quinoline nucleus.

3. In a process of making photographic images wherein a light-sensitive photographic emulsion is exposed to radiation at a temperature below about −180° C. to produce a latent image, and said latent image is developed to a silver image: the improvement which comprises employing in said process a negative, unfogged photographic silver halide emulsion in which the silver halide grains thereof have adsorbed thereto a sufficient amount of a quinoline monomethine cyanine dye to effectively increase the speed of said silver halide when exposed at a temperature below about −180° C.

4. In a process of making photographic images wherein a light-sensitive photographic emulsion is exposed to radiation at a temperature below about −180° C. to produce a latent image, and said latent image is developed to a silver image: the improvement which comprises employing in said process a negative, unfogged photographic silver halide emulsion in which the silver halide grains thereof have adsorbed thereto a dye selected from the group consisting of 1,1′,3,3′-tetramethyl-2,2′-cyanine dye salt; a 3,3′-diethylthiacarbocyanine dye salt; 2-(p-dimethyl-aminostyryl)-1-methyl pyridinium dye salt; 1,1′-diethyl-2,2′-cyanine dye salt; 1,1′-dimethyl-2,2′-cyanine dye salt; 1,1′-diethyl-2,4′-cyanine dye salt; and, 1-methyl-1′,9-diethyl-2,2′-cyanine dye salt; said silver halide having a sufficient amount of said dye adsorbed thereto to effectively increase the speed and contrast of said silver halide when exposed at a temperature of −180° C.

5. The process of making photographic images as defined in claim 5 wherein said dye is adsorbed onto said silver halide in a concentration sufficient to give monomolecular layer coverage of the silver halide grains.

6. In a process of making photographic images wherein a light-sensitive photographic silver halide emulsion is exposed to radiation at a temperature below about −180° C. to produce a latent image, and said latent image is developed to a silver image: the improvement which comprises employing in said process an unfogged cubic-regular grain silver bromoiodide gelatin emulsion, the grains of said emulsion having a size of about 0.2 microns, said grains having adsorbed thereto a monomolecular layer coverage of a 1,1′-diethyl-2,2′-cyanine dye salt.

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