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PHOTOGRAPHIC PROCESSES

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U.S. Cl. 96—107 8 Claims

ABSTRACT OF THE DISCLOSURE

Silver halide grains, having certain methine sensitizing dyes adsorbed thereto, are rendered sensitive to infrared radiation longer than about 2.0 micron by cooling the grains to below about —180° C., and uniformly exposing the cooled grains to radiation having a wavelength from about 370 to about 460 nm. to produce a developable latent image. An imagewise infrared Herschel exposure of the cooled grains causes imagewise destruction of the developable latent image.

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

James, in U.S. Pat. application 822,670 filed May 7, 1969, and in Photographic Science and Engineering, vol. 14, No. 1, January-February 1971, pp. 84–86, shows that the sensitivity and contrast of photographic silver halide emulsions to be exposed at low temperatures (i.e., below about —180° C.) can be increaed by adsorbing certain methine dyes to the silver halide grains. The useful methine dyes described by James are those in which the highest occupied electronic energy level of the unaggregated dye at room temperature is more positive than the highest occupied energy level of the valence band of the silver halide, and the lowest vacant electronic energy level of the dye, in its unaggregated form at room temperature, is more positive than the conduction band of the silver halide. The dyes are used in relatively large concentrations with best results being obtained when the grains have a monolayer coverage of the dye.

James et al. in Photographic Science and Engineering, vol. 4, No. 4 (1963), describe the use of the Herschel effect on a low temperature silver halide emulsion as a means for detecting infrared radiation up to about 1.8 microns, and suggests there might be some utility in carrying out the process to detect I.R. radiation of up to 2.0 microns in wavelength. No disclosure is known in the art for effectively increasing the sensitivity of a low temperature silver halide emulsion to infrared radiation of greater than 2.0 microns.

Accordingly, this invention is directed toward photographic processes in which silver halide photographic emulsions are exposed at low temperatures. In one aspect the present invention is directed to photographic processes producing a silver halide emulsion having increased infrared sensitivity when exposed at low temperatures on the order of about —180° C. Still another aspect of the present invention is to provide photographic processes useful for detecting long wavelength infrared radiation, e.g., infrared radiation having wavelengths from 2.0 to about 3.5 microns. Other aspects of the invention will be apparent from the disclosure herein and the appended claims.

In accordance with this invention, a photographic process is provided for increasing the infrared sensitivity of silver halide grains maintained at a temperature below about —180° C., said grains having adsorbed thereto a methine sensitizing dye, the highest occupied electronic energy level of said dye, in its unaggregated form at room temperature, 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, in its unaggregated form at room temperature, being more positive than the conduction band of the silver halide, said dye trapping electrons at a depth of not more than .7 ev. below the conduction band of the silver halide at temperatures below about —180° C., the silver halide grains having a sufficient amount of the dye adsorbed thereto to effectively increase the speed of the silver halide when exposed at a temperature below about —180° C., which comprises:

(1) cooling the photographic silver halide emulsion to a temperature below about —180° C.; and,

(2) uniformly exposing the cooled emulsion to blue light of a wavelength of from about 370 to about 460 nm. for sufficient time to produce a latent image having a developable density.

Preferably, the overall low temperature exposure to radiation of about 370 to about 460 nm. is sufficient to produce a developable density of at least 1.0 or higher. The latent image produced by the overall exposure can be removed by a long wavelength infrared imagewise exposure while the emulsion is maintained at the low temperature. The emulsion is not warmed to a temperature substantially above about —180° C. between the overall exposure and the imagewise infrared exposure.

The low temperature infrared exposure destroys the latent image produced by the low temperature overall exposure, the amount of destruction of the latent image varying with the intensity and wavelength of the infrared radiation striking the emulsion. In view of the James et al. disclosure, it was very surprising that the present process renders emulsions sensitive to infrared radiation extending well beyond the 2.0 micron limit.

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, in its unaggregated form at room temperature, 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, in its unaggregated form at room temperature, 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, vol. 11, No. 3, p. 129 (1967) and Tani, Kikuchi and Honda in Photographic Science and Engineering, vol. 2, p. 80 (1968).

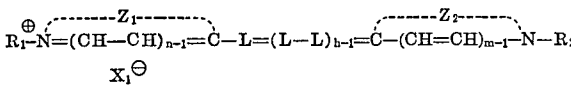
At temperatures below about —180° C., the dyes employed herein trap electrons at a depth of not more than .7 ev., and preferably not more than .4 ev., below the conduction band of the silver halide. These calculations can be made by the procedure described by Berry in The Journal of Photographic Science, 1970, vol. 18, No. 5, pp. 169 and 174.

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), pp. 19–21, 264 and 265, and Tani, Kikuchi and Honda, Photographic Science and Engineering, volume 12, No. 2 (1968) p. 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 valence band of approxi-

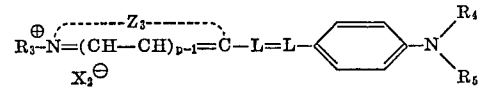
mately —6.0 ev. relative to 0 for vacuum, with the electronic energy of the bottom of the conduction band of the silver bromide being approximately —3.5 ev. Further description of the mechanism for calculating the highest occupied energy level in the valence band and bottom conduction band of silver halides is given in Grundlagen der photographichen Prozesse mit Silberhalogen-iden; Band 3, 1968, Akademische Verlagsgesellschaft, pages 1068–1071.

Any of the methine dyes, including the styryl and cyanine methine dyes, can be employed in the practice of the invention, provided the dyes meet the criteria given above. Especially good results are obtained with methine dyes which meet the above criteria and have at least one of the following formulas:

Formula 1



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 1 to 4 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 1 to 4 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, 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 1 to 6 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-toluenesulfonate and which may be combined in R_1 or R_3 when the dye is a betaine; Z_1, Z_2 and Z_3 each represents the non-metallic atoms necessary to complete the same or different 5- to 6-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, 4-methoxybenzothiazole, 5-methoxybenzothiazole, 6-methoxybenzothiazole, 5-iodobenzothiazole, 6-iodobenzothiazole, 4-ethoxybenozthiazole, 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, 7-methoxynaphtho[2,3-d]thiazole, 4'-methoxythianaphtheno-7',6',4,5-thiazole, etc.; an oxazole nucleus, e.g., 4-methloxazole, 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-d]oxazole, naphtho[1,2-d]oxazole, etc.; a selenazole nucleus, e.g., 4-methylselenazole, 4-phenylselenazole, benzoselenazole, 5-chlorobenzoselenazole, 5-methoxybenzoselenazole, 5-hydroxybenzoselenazole, 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'-dimethyl-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

Dyes particularly useful in carrying out the method of the present invention for detecting infrared radiation of wavelengths from about 2.0 to about 3.5 microns are

1,1'-diethyl-2,2'-cyanine chloride,
1,1',3,3'-tetramethyl-2,2'-cyanine p-toluenesulfonate,
3,3'-diethyl-9-methylthiacarbocyanine bromide,
3,3'-diethylthiacarbocyanine p-toluenesulfonate,
1,1'-diethyl-2,4'-cyanine chloride, and
1,1'-dimethyl-2,2'-cyanine p-toluenesulfonate.

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 .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% 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 .02 to .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. Conven-

tional negative, developing-out, unfogged silver halide emulsions are used in this invention. Advantageously, the average silver halide grain size can be up to .8 micron and preferably is up to about .5 micron with the very best results being obtained with small cubic grains, the edges of which are on the order of about .2 micron. Silver bromoiodide and silver bromide emulsions are preferred.

In order to obtain the desired results of this invention, it is advantageous to employ silver halide grains which are free from chemical sensitizers, such as sulfur sensitiziers or noble metal salt sensitizers, and chemical foggants.

The silver halide grains employed in this invention can be coated on any suitable support, such as paper, cellulose acetate or poly(ethylene-terephthalate) supports, and the grains can be dispersed in suitable binders, such as gelatin. If desired, the silver halide grains can be vacuum deposited on a suitable support.

The silver halide emulsions used herein can contain antifoggants, stabilizers, hardeners and plasticizers described and referred to in Beavers U.S. Pat. 3,039,873 (1962) col. 10–13.

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.

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

EXAMPLE 1

A gelatin silver iodobromide emulsion is prepared substantially as described in French Pat. 1,497,202 without chemical sensitization. The crystal habit of the silver halide grains in this preparation is cubic (the edges being about .2 micron) and the emulsion is coated on a cellulose acetate base with 100 mg. Ag/sq. ft. 200 mg. gelatin/sq. ft. and 800 mg./mole Ag of 1,1'-diethyl-2,2'-cyanine chloride. One 35 mm. strip of this photographic film is exposed for 1 minute, while immersed in liquid nitrogen (77° K.), to a 200 watt tungsten lamp filtered by one Wratten 36 filter, one Wratten 38A filter (this filter combination limits the exposure to the 370–460 nm. spectral region). While still immersed in liquid nitrogen a small portion of this exposed film is then irradiated for 2 minutes with a tungsten source filtered with a germanium filter which limited the exposure to wavelengths longer than 1.7μ. The energy hitting the film is 120 mw./sq. cm. The exposed film is then developed for 12 minutes at 20° C. in a solution of N-methyl-p-aminophenol sulfate 2.5 g., ascorbic acid 10.0 g., sodium metaborate 35.0 g., potassium bromide 1.0 g., and water to make 1 liter. It is then fixed for 3 minutes, washed and dried. Densities are read on a densitometer through a red filter. The measured density in the area not irradiated with the radiation having wavelengths longer than 1.7μ is .97. The density in the area irradiated with the radiation with wavelengths greater than 1.7μ is .06. Percent destruction of the latent image is 94. Generally similar results are obtained when the 1,1'-diethyl-2,2'-cyanine chloride is replaced with similar quantities of 1,1',3,3' tetramethyl-2,2'-cyanine pts, 3,3'-diethyl - 9 - methylthiacarbocyanine bromide, 3,3'-diethylthiacarbocyanine pts, 1,1'-diethyl-2,4'-cyanine chloride and 1,1'-dimethyl-2,2'-cyanine pts ("pts" refers to p-toluenesulfonate).

EXAMPLE 2

The photographic film described in Example 1 is used for the exposure described in Example 2. A strip of this photographic film is exposed for 40 seconds while immersed in liquid nitrogen (77° K.), to a 200 watt tungsten lamp filtered by one Wratten 36 filter, one Wratten 38A filter. While still immersed in liquid nitrogen a small portion of this exposed film is then irradiated for 20 minutes with a tungsten source filtered with a germanium filter and a Kodak Infrared Interference filter series 420. This filter combination limits the exposure to wavelengths longer than 2.2μ. The energy hitting the film is 30 mw./sq. cm. The exposed film is then developed, fixed, washed and dried as in Example 1. The measured density in the area not irradiated with the radiation having wavelengths longer than 2.2μ is 1.00. The density in the area irradiated with the radiation with wavelengths greater than 2.2μ is .34. Percent destruction of the latent image is 66.

EXAMPLE 3

The photographic film described in Example 1 is used for the exposure described in Example 3. A strip of this photographic film is exposed for 20 seconds while immersed in liquid nitrogen (77° K.), to a 200 watt tungsten lamp filtered by one Wratten 36 filter and one Wratten 38A filter. While still immersed in liquid nitrogen a small portion of this exposed film is then irradiated for 40 minutes with a neon laser tuned to a wavelength of 3.39μ. A 2.2μ cuton filter is used to insure that no shorter wavelength can reach the film. The energy hitting the film is 31 mw./cm.^{2}. The exposed film is then developed, fixed, washed and dried as in Example 1. The measured density in the area not irradiated with the 3.39μ radiation is 1.10. The density in the area irradiated with the 3.39μ radiation is 1.00. Percent destruction of the latent image is 9.

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.

We claim:

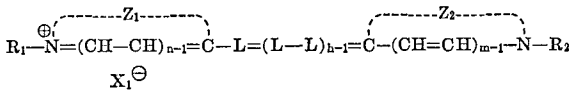
1. A photographic process for increasing the infrared sensitivity of silver halide grains maintained at a temperature below about —180° C., said grains having adsorbed thereto a methine sensitizing dye, the highest occupied electronic energy level of said dye, in its unaggregated form at room temperature, 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, in its unaggregated form at room temperature, being more positive than the conduction band of the silver halide, said dye trapping electrons at a depth of not more than .7 ev. below the conduction band of the silver halide at temperatures below about —180° C., the silver halide grains having a sufficient amount of th dye adsorbed thereto to effectively increase the speed of the silver halide when exposed at a temperature below about —180° C., which comprises:

(1) cooling the photographic silver halide emulsion to a temperature below about —180° C.; and,

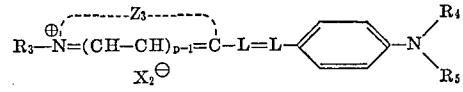
(2) uniformly exposing the cooled emulsion to blue light of a wavelength of from about 370 to about 460 nm. for sufficient time to produce a latent image having a developable density.

2. A photographic process for increasing the infrared sensitivity of a photographic silver halide emulsion maintained at a temperature below about —180° C., said emulsion comprising silver halide grains having adsorbed thereto a methine dye, the highest occupied electronic energy level of said dye, in its unaggregated form at room temperature, 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, in its unaggregated form at room temperature,

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 conduction band of the silver halide, said dye trapping electrons at a depth of not more than .7 ev. below the conduction band of the silver halide at temperatures below about —180° C., said dye having at least one of the following formulas:



and



wherein *h*, *m*, *n* and *p* each represents an integer of from 1 to 2; L represents a methine linkage; R_1, 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 1 to 6 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 5- to 6-membered heterocyclic nucleus of the type used in methine dyes, the silver halide grains having a sufficient amount of the dye adsorbed thereto to effectively increase the speed of the silver halide when exposed at a temperature below about —180° C., which comprises:

(1) cooling the photographic silver halide emulsion to a temperature below about —180° C.; and

(2) uniformly exposing the cooled emulsion to blue light of a wavelength of from about 370 to about 460 nm. for sufficient time to produce a latent image having a developable density.

3. The process as defined in claim **2** 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, a selenazole nucleus, and a quinoline nucleus.

4. The process as defined in claim **2** wherein said dye is adsorbed onto said silver halide in a concentration sufficient to give monomolecular layer coverage of the silver halide grains.

5. A photographic process for rendering a light-sensitive photographic silver halide emulsion maintained at a temperature below about —180° C. sensitive to infrared radiation of a wavelength from about 2.0 to about 3.5 microns, said emulsion comprising silver halide grains having adsorbed thereto a methine sensitizing dye, said dye selected from the group consisting of

1,1-diethyl-2,2'-cyanine dye salt;
1,1',3,3'-tetramethyl-2'-cyanine dye salt;
3,3'-diethyl-9-methylthiacarbocyanine dye salt;
3,3'-diethylthiacarbocyanine dye salt;
1,1'-diethyl-2,4'-cyanine dye salt; and
1,1'-dimethyl-2,2'-cyanine dye salt

which comprises:

(1) cooling the photographic silver halide emulsion to a temperature below about —180° C.; and

(2) uniformly exposing the cooled emulsion to blue light of a wavelength of from about 370 to about 460 nm. for sufficient time to produce a latent image having a developable density of about 1.0.

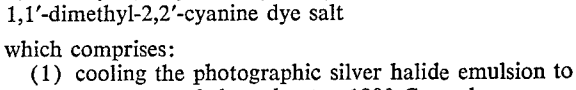
6. A photographic process for rendering a light-sensitive photographic silver halide emulsion maintained at a temperature below about —180° C. sensitive to infrared radiation of a wavelength from about 2.0 to about 3.5 microns, said emulsion comprising an unfogged cubic regular-grain silver bromoiodide gelatin emulsion, the grains of said emulsion having a size of about 0.2 micron, said grains having adsorbed thereto a monomolecular layer coverage of a 1,1'-diethyl-2,2'-cyanine dye salt, which comprises:

(1) cooling the photographic silver halide emulsion to a temperature below about —180° C.; and

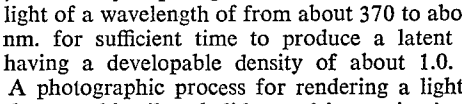
(2) uniformly exposing the cooled emulsion to blue light of a wavelength of from about 370 to about 460 nm. for sufficient time to produce a latent image having a developable density of at least about 1.0.

7. In a photographic process in which light-sensitive silver halide grains are cooled to a temperature below about —180° C., uniformly exposed to radiation having a wavelength of about 370 to about 460 nm. to produce a developable latent image and, while maintaining the temperature of the grains below about —180° C., giving said grains an imagewise Herschel exposure to infrared radiation to at least partially destroy said latent image, said silver halide grains being essentially free from chemical sensitizers and having an average grain size up to about .8 micron, the improvement which comprises: employing in said process silver halide grains which have adsorbed thereto a methine sensitizing dye, the highest occupied electronic energy level of said dye, in its unaggregated form at room temperature, 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, in its unaggregated form at room temperature, more positive than the conduction band of the silver halide, said dye trapping electrons at a depth of not more than .7 ev. below the conduction band of the silver halide at temperatures below about —180° C., said silver halide grains 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.

8. In a photographic process in which light-sensitive silver halide grains are cooled to a temperature below about —180° C. uniformly exposed to radiation having a wavelength of about 370 to 460 nm. to produce a latent image developable to a density of at least 1.0 and, while maintaining the temperature of the grains below about —180° C., giving said grains a Herschel exposure to infrared radiation to at least partially destroy said latent image, said silver halide grains being free from chemical sensitizers, and the halide of said silver halide bromide or bromoiodide, said grains having an average grain size up to about .5 micron, the improvement which comprises: employing in said process silver halide grains which have adsorbed thereto a methine sensitizing 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, in its unaggregated form at room temperature, more positive than the conduction band of the silver halide, said dye trapping electrons at a depth of not more than .7 ev. below the conduction band of the silver halide at temperatures below about —180° C., said dye having at least one of the following formulas:



and



wherein *h*, *m*, *n* and *p* each represents an integer of from 1 to 2; L represents a methine linkage; R_1, 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 1 to 6 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 5-

to 6-membered heterocyclic nucleus of the type used in methine dyes, said silver halide grains 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.

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U.S. Cl. X.R.

96—45.2, 94, 120; 250—65 F