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THERMAL RESENSITIZATION OF DESENSITIZED SILVER HALIDE PHOTOGRAPHIC EMULSIONS

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12 Claims. (Cl. 96—65)

This application is a continuation-in-part application of our copending application Serial No. 812,847, filed May 13, 1959, now abandoned.

This invention relates to photographic silver halide emulsions, and more particularly, to the processing of photographic elements having coated thereon photographic silver halide emulsions.

Photographic silver halide emulsions have been widely used for the purpose of reproducing original scenes, both by amateur photographers and those professionally trained. The reason for the wide acceptance of silver halide photography has been due to the high amplification effect which is produced by photographic development of silver halide grains which have only been briefly exposed to relatively small energy quanta. This multiplication or amplification is similar in effect to that obtained in a radio receiver or other electronic device which receives a weak signal and amplifies it thousands, or perhaps millions, of times. Although the amplification in silver halide photography is quite substantial, frequently this effect can be obtained while retaining the valuable contrast and definition characteristics present in original scene, or document.

The high speed of silver halide photography does present serious problems in handling the sensitive material before photographic exposure and development. Thus, elaborate precautions must be taken in order to avoid accidental exposure of the sensitive material. These precautions must be taken both by the amateur and by the professional photofinishers, who might use the sensitive material in large quantities in various photocopying devices.

It is an object of the invention to provide a new method of sensitizing photographic silver halide emulsions which have been rendered substantially insensitive to X-ray, ultraviolet, visible or infrared radiation by treatment with various chemical desensitizing agents.

Another object of the invention is to provide novel desensitized photographic silver halide emulsions which can be handled under brighter safelights than normal or even, in some cases, in ordinary room light or normal daylight.

It is still another object of the invention to provide a novel thermographic reproduction method.

It is likewise an object of this invention to provide a new process for resensitizing a previously desensitized emulsion to the recording of latent images by a factor of at least 10 times.

These and other objects of the invention are accomplished by heat treating a photographic element having coated thereon a photographic silver halide emulsion that had been chemically desensitized to the recording of latent images, and by such heat treating significantly increasing the sensitivity to the recording of latent images of the silver halide emulsion.

According to the present invention, photographic silver halide emulsions which have been chemically desensitized to the recording of latent images are subjected to an elevated temperature of at least about 100° C. for a short time before photographic exposure. This heat treatment can be utilized to restore a substantial part or substantially all of the sensitivity to the formation of latent images exhibited by the photographic silver halide emulsions prior to treatment with the chemical desensitizing agent. Temperatures which have been found particularly useful in our invention vary from about 100° C. to 300° C.

The heat treatment period for resensitizing the ability of the present photographic elements to the formation of latent images can be widely varied, periods of time up to about 5 minutes are generally suitable, and periods of time up to about one minute are preferred. Higher temperatures require shorter treatment periods. The most expeditious time and temperature for a given material can be easily determined by one skilled in the art by running a series of tests varying either the temperature or time of treatment, but maintaining one of these constant during the testing cycle. Desensitized photographic elements of the invention can be resensitized with a wide variety of heating means including infrared lamps, heated enclosures, hot platens, heater bars, heated rollers and the like. Infrared lamps can be utilized to selectively resensitize the photographic elements, such a heat treating being suitably effected through an original in contact with the emulsion surface of the photographic element. The selectively resensitized areas can then be flashed to produce a developable latent image. Reference is made to Miller, U.S. Patent No. 2,740,896, for illustrative apparatus that can be utilized to thermally resensitize the photographic elements of the invention. While it has been previously known that the sensitivity of certain photographic silver halide emulsions could be temporarily increased by briefly heating the emulsion prior to exposure, the gains in speed have been relatively small and usually only temporary. In the present invention we are concerned with increasing the sensitivity of photographic elements to record latent images at least 10 times (1 log E). It was surprising to find that emulsions which had been rendered substantially insensitive to the formation of latent images by X-ray, ultraviolet, visible and infrared radiation could be thermally resensitized to the recording of latent images by substantial factors.

The photographic emulsions useful in practicing our invention comprise the conventional negative-type, developing out, unfogged photographic silver halide emulsions, such as silver chloride, silver bromide, silver bromoiodide, silver chlorobromide, silver chlorobromoiodide, and the like. The present emulsions generally have fog levels less than about .5 when developed for 5 minutes at 68° F. in Developer B described in Example 2 below. Also, the present emulsions, before desensitization, generally have sensitivities of at least about 3 log E, and preferably in the range of about 0 to $\overline{1.5}$ log E, with satisfactory results being obtained with emulsions having sensitivities up to about $\overline{3}$ log E, E being the exposure in meter-candle-seconds required to produce a density of .2 above fog when developed for 5 minutes at 68° F. in Developer B.

The silver halides can be dispersed in conventional photographic vehicles, such as gelatin, hydrolyzed polyvinyl esters, hydrolyzed cellulose esters, albumins, agar-

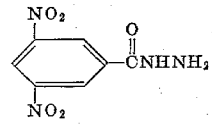
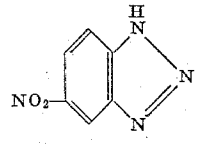
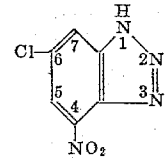
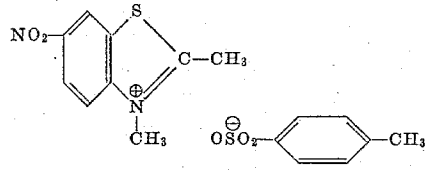
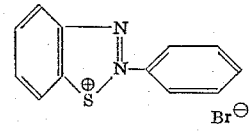
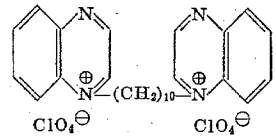
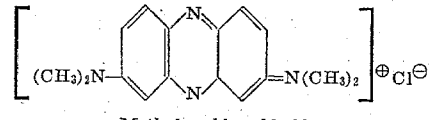
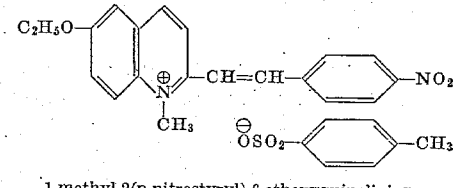
agar, gum arabic, etc. to form the present emulsions. Gelatin is preferred.

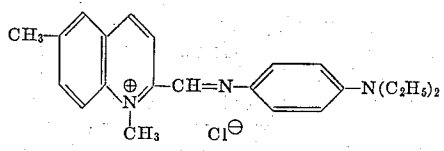
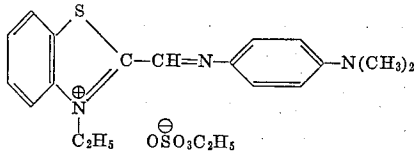
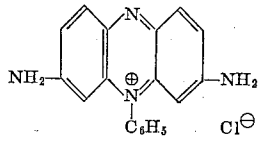
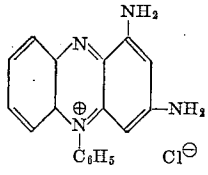
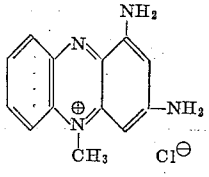
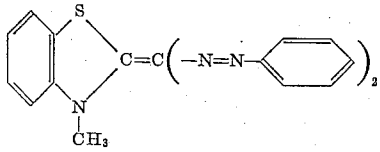
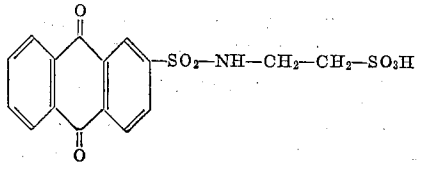
While the emulsions useful in our invention can be coated on many conventional, relatively thin (e.g., 1 to 10 mils) photographic supports or films, it is apparent that photographic supports should not be used which soften, stick, or become dimensionally unstable at the temperature used to resensitize the emulsions. For this reason, fibrous supports such as paper, higher melting polyester resin supports such as polyethylene terephthalate and polymers of cyclohexanedimethanol and terephthalic acid as described by Kibler et al. in U.S. Patent No. 2,901,466, or other photographic supports not adversely affected by the present elevated processing temperatures, are useful in practicing our inventon.

Photographic silver halide emulsions which can be used in our invention also include photographic emulsions adapted for use in X-ray photography. It has been found that the latent image formation of such emulsions can be effectively inhibited and then treated according to the method of our invention to restore their sensitivity to X-rays.

The photographic silver halide emulsions according to our invention can contain a wide variety of the conventional chemical desensitizers that inhibit the ability of the emulsions to form latent images. The present photographic silver halide emulsions are made substantially insensitive to the formation of latent images with chemical desensitizers to radiations of at least about 1 to 1200 mμ and suitably within the wave lengths of gamma radition and infrared radiation (i.e. about 1×10^{-3} to 1×10^{5} mμ). Such treated emulsions can be exposed to X-ray radiation up to 100 roentgens, and preferably up to 1000 roentgens, without having a density greater than .1 when developed for 5 minutes at 68° F. in Developer B. Some suitable chemical desensitizers are especially active and hence require only a few milligrams per mole of silver halide to decrease the emulsion photosensitivity by a large factor. Other chemical desensitizers are less efficient and may require several grams in order to reduce effectively the photosensitivity of the silver halide emulsion to an extent sufficient to prevent fogging of the silver halide emulsion upon exposure to ambient radiation. Generally we utilize between about .01 to 5 grams of desensitizer per mole of silver halide in the emulsion. The optimum amount utilized for a particular densitizer can be readily ascertained by one skilled in the art. Typical desensitizers which can be present in the photographic silver halide emulsions of our invention include heavy metal salts, such as mercury salts, rhodium salts, etc. Other chemical desensitizers which can be used in our invention comprise heterocyclic compounds containing at least one hetero sulfur and/or nitrogen atom. Heterocyclic desensitizers containing at least one benzene ring, and desirably containing at least one nitro substituent attached to the benzene ring, are especially useful. Typical of such organic desensitizers are benzotriazole compounds containing a nitro substituents on the benzene ring of the benzotriazole nucleus, e.g., 5-nitrobenzo-1,2,3-triazole, 4-nitrobenzo-1,2,3-triazole, etc. (including their halogen substituted derivatives, such as 5-chloro-, 6-chloro-, etc.). Non-heterocyclic aromatic desensitizers containing at least one nitro substituent such as 3,5-dinitrobenzhydrazide and the like are also useful. Another group of chemical desensitizers comprise a class of dyes known as styryl dyes which contain at least one nitro substituent attached to a benzene ring. Other chemical desensitizers include anil and safranine dyes. Anthraquinone dyes containing a sulfoalkylaminosulfone radical can also be used to desensitize photographic silver halide emulsions useful in practicing our invention.

The following compounds are representative of chemical desensitizers which are useful in treating the photographic silver halide emulsions of our invention to inhibit their ability to form latent images. The compound numbers below are referred to in the detailed examples below.

Compound No.	Desensitizer
1	$HgCl_2$ Mercuric chloride
2	$(NH_4)_3RhCl_6$ Triammonium hexachlororhodite
3	 3,5-dinitrobenzhydrazide
4	 5-nitrobenzo-1,2,3-triazole
5	 4-nitro-6-chlorobenzotriazole
6	 2,3-dimethyl-6-nitrobenzothiazolium p-toluenesulfonate
7	 2-phenylbenzo-1,2,3-thiadiazolium bromide
8	 N,N'-decamethylene-bis(quinoxalinium)perchlorate
9	 Methylene blue chloride
10	 1-methyl-2(p-nitrostyryl)-6-ethoxyquinolinium p-toluenesulfonate

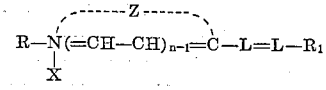
Compound No.	Desensitizer
11	 2-(p-diethylaminophenyliminomethyl)-1,6-dimethylquinolinium chloride
12	 2-(p-dimethylaminophenyliminomethyl)-3-ethylbenzothiazolium ethosulfate
13	 Phenosafranine (chloride)
14	 Pinakryptol green (chloride)
15	 1,3-diamino-5-methylphenazinium chloride
16	 3-methyl-2-bis(phenylazo)methylene benzothiazoline
17	 Anthraquinone-2-sulphotauride

Patents which describe photographic silver halide desensitizers useful in treating the silver halide emulsions of our invention include the following, for example.

Schuloff, U.S. 1,653,314, granted December 20, 1927
Homolka, U.S. 1,760,756, granted May 27, 1930
Müller et al., U.S. 2,196,162, granted April 2, 1940
Kendall et al., U.S. 2,541,472, granted February 13, 1951
Kendall et al., U.S. 2,669,515, granted February 16, 1954
Horwitz, U.S. 2,794,802, granted June 4, 1957
Groves, British 465,343, accepted April 30, 1937
Compagnie, French 1,049,896, issued August 26, 1953, and addition 64,756, issued June 29, 1955
Compagnie, French 1,092,537, issued November 10, 1954

Compound 7 above was prepared according to the method described by A. Burowoy, A. Chaudhuri and C. E. Vellins in "Journal Chemical Society" (London), page 90 (1956). Compound 11 is described by Mees, "The Theory of the Photographic Process," 1st ed., (Macmillan), page 1043 (page 422 of 2nd ed.), and by Kendall et al., British Patent 447,109, accepted May 4, 1936. Compound 16 can be prepared as described in French Patent 1,049,896 (see French 1,092,537 for formula).

Especially useful chemical desensitizers which are described in several of the afore-mentioned patents include the cyclammonium quaternary salts represented by the following general formula:

(A) 

wherein R represents an alcohol radical, i.e., a substituted or unsubstituted alkyl group, such as methyl, ethyl, propyl, butyl, ethoxycarbonylmethyl, β-hydroxyethyl, etc., R_1 represents an aryl group, such as phenyl, or phenyl substituted by common organic radicals, such as hydroxyl nitro, amino, alkylamino, dialkylamino, methyl, ethyl, ethoxyl, methoxyl, etc., L represents a methine group, i.e., a —CR'=group where R' represents a hydrogen atom or an alkyl group, such as methyl, ethyl, etc., X represents an acid radical, such as chloride, bromide, iodide, perchlorate, benzenesulfonate, p-toluenesulfonate, methylsulfate, ethylsulfate, etc., *n* represents a positive integer of from 1 to 2, and Z represents the non-metallic atoms necessary to complete a heterocyclic nucleus containing at least one sulfur and/or nitrogen atom and from 5 to 6 atoms in the heterocyclic ring, such nuclei being well-known to those skilled in the art. It is to be understood that the styryl dyes embraced by Formula A above contain at least one benzene nucleus to which is attached at least one nitro group. Typical nuclei defined by Z include benzothiazole, quinoline, benzoxazole, indolenine, etc., which can contain simple substitutents on the benzene ring thereof, such as methyl, ethyl, methoxy, ethoxyl, hydroxyl, amino, etc.

The photographic silver halide emulsions of the invention can contain the usual emulsion addenda such as chemical sensitizers, antifoggants, plasticizers, hardeners, coating aids, and the like. Gold and sulfur sensitized emulsions are particularly useful. For example, sensitizing sulfur compounds can be added as described in Sheppard U.S. Patent No. 1,574,944, Sheppard et al. U.S. Patent No. 1,623,499, and Sheppard at al. U.S. Patent No. 2,410,689. The emulsions are typically sensitized with gold salts as described in Waller et al. U.S. Patent No. 2,399,083 and Damschroder et al. U.S. Patent No. 2,642,-361. Suitable sensitizing gold compounds include potassium chloroaurite, potassium aurithiocyanate, potassium chloroaurate, auric trichloride and 2-aurosulfobenzothiazole methochloride.

In carrying out the present thermographic process, the desensitizer in the emulsion inhibited against the formation of latent images is not destroyed or removed (e.g. by sublimation) from the photographic element during heating.

The following examples further illustrate preferred embodiments of the present invention.

EXAMPLE 1

A 35-mm. strip of a photographic gelatino-, fine-grain, negative-type, developing out silver bromoiodide emulsion containing a desensitizing agent or chemical latent image inhibitor in the amount shown in Table A below coated on a glossy single-weight, baryta-coated paper stock at a coverage of approximately 475 square feet per

mole of silver, was pulled at a rate shown in the following table over a 2.5-inch wide curved brass bar operating at a temperature of about 250° C. A similar coating containing no densensitizer served as a control and was heat-treated in a similar manner. The two heat-treated strips, along with a non-heat-treated latent image inhibited emulsion coated strip, were then exposed for 4 seconds to a 500-watt, 3000° K. light source (log E max.=3.89) in an intensity scale sensitometer. The exposed strips were then developed for one minute at 68° F. in a developer having the following composition:

Developer A

	Grams
N-methyl-p-aminophenol sulfate	3.1
Sodium sulfite, desiccated	45.0
Hydroquinone	12.0
Sodium carbonate, desiccated	67.5
Potassium bromide	1.9

Water to make two liters.

The developed strips were then fixed, washed and dried in the usual manner. The sensitometric strips were then read on a densitometer. The untreated desenitized emulsion coatings showed no visible image after exposure in the sensitometer and processing in the Developer A described above. The coatings containing the desensitizers numbered 2, 3, 8, 10 and 12 showed no fog, even after 4 hours exposure to daylight (150 foot-candles) and processing in Developer A. Table A below identifies the desenitizer used in each of the coatings (the numbers corresponding to those given above), the concentration of the desensitizer in terms of grams per mole of silver in the emulsion, the paper travel speed and the density measurements and speed figures in terms of log E at D equal to 1.0 (except for Compound 8, for which the speed reading was taken at D equal to 0.6).

TABLE A

Desensitizer	Concentration (g./mole Ag)	Paper travel speed (ft./min.)	$D_{min.}$	$D_{max.}$ (reflection)	Log E at D=1.0
Control		4	0	2.3	2.74
1	0.1	4	0	2.3	2.90
2	0.1	4	0.02	2.3	2.76
3	1.0	4	0	2.3	2.65
4	3.0	4	0	2.3	2.76
5	3.0	4	0	2.3	2.87
6	3.0	4	0.01	2.2	3.06
7	1.25	4	0	2.2	3.08
8	0.4	12	0	0.8	[1] 3.94
9	0.25	4	0.05	2.1	2.98
10	0.25	4	0.02	2.3	2.84
11	0.25	5	0.04	2.1	3.20
12	0.25	5	0.02	2.1	2.96
13	0.25	5	[2]	2.2	2.84
14	0.25	5	[2]	2.2	2.94
15	0.25	5	[2]	2.3	2.84
16	1.00	4	0	2.1	3.56

[1] (D equal to 0.6). [2] Slight Stain.

Emulsions desensitized with other densitizing compounds can be treated according to the method described in Example 1 to restore the sensitivity of the emulsions to the recording of latent images to substantially the level present prior to their densensitization. The heat treatment need not be to the entire surface of the desensitized photographic emulsion as described in Example 1, thus providing a means of obtaining copies of an original document, or photographic print, which contains portions highly absorptive of infrared energy and portions which do not absorb substantial quantities of infrared energy (i.e., substantially nonabsorptive). This latter embodiment is described in more detail in Example 5.

EXAMPLE 2

The effect of various concentrations of the desensitizer, 4-nitro-6-chlorobenzotriazole (Compound 5), on the latent image formatoin of a photographic emulsion to visible light and X-ray wave lengths was tested. Portions of a gold and sulfur sensitized, negative-type, developing out gelatino-silver chlorobromide emulsions containing varying levels of Compound 5, as well as control samples containing no desensitizer, were coated on 4 mil thick film bases of polyethylene terephthalate at a coverage of 137 mg. of silver per square foot. Samples of the prepared films were then exposed to visible light at $\frac{1}{1000}$ second in an intensity scale sensitometer and thereafter developed for 5 minutes at 68° F. in Developer B below, and fixed in hypo in the usual manner. Other samples were resensitized to the recording of latent images by heating at 145° C. for 5 seconds before exposing in the sensitometer and developing. The heating was effected by contacting the emulsion side of the films with a heated platen.

Developer B

	Grams
N-methyl-p-aminophenol sulfate	2.2
Sodium sulfite, desiccated	72.0
Hydroquinone	8.8
Sodium carbonate, desiccated	130.0
Potassium bromide	4.0

Water to make one liter.

The results of the sensitometric tests are summarized by the data set out in Table B below.

TABLE B

Compound 5 Concentration (g./mole Ag)	No heat treatment			5 seconds at 145° C.		
	Relative speed	γ	Fog	Relative speed	γ	Fog
0	100	3.52	.05	186	2.78	.13
1	4.50	4.30	.05	65	2.26	.07
1.6	2.95	4.40	.05	52	2.88	.07
2.2	2.25	4.20	.05	39	2.92	.06
3.0	1.75	3.00	.05	21.5	2.60	.06

As can be observed from the data set out in Table B, the brief heat treatment substantially resensitized the emulsions to the recording of latent images by factors of more than 1 log E. Other samples of the prepared films were flashed with 100 kv. X-rays at various Roentgen levels, developed in Developer B described above and fixed in hypo in the usual manner. The developed densities for the various films after X-ray exposures are summarized by the data set out in Table C below.

TABLE C.—Developed Densities After X-Ray Exposure

Compound 5 Concentration (g./mole Ag)	0 R.	50 R.	100 R.	200 R.	500 R.	1,000 R.
0	.06	2.86	3.77	4.0+	4.0+	4.0+
1	.05	.11	.18	.40	1.22	2.44
1.6	.05	.06	.06	.10	.28	.67
2.2	.06	.05	.06	.07	.14	.27
3.0	.05	.05	.05	.05	.08	.15

EXAMPLE 3

Several samples of gold and sulfur sensitized negative-type developing out gelatino-silver chlorobromide emulsions containing one gram of the desensitizer, 4-nitro-6-chlorobenzotriazole (Compound 5), per mole of silver halide, were coated on 4 mil thick polyethylene terephthalate film base at coverage of 300 mg. of silver per square foot and dried. The dried coating samples were then subjected to various temperatures for the time inter-

vals listed below, then exposed in an intensity scale sensitometer and processed as described in Example 2.

TABLE D

		Relative speed	γ	Fog
Control, no desensitizer, no heating		100	2.8	.06
Control, desensitizer, no heating		3.6	4.0	.05
Heat treated desensitized films				
Time (sec.)	Temp. (° C.)			
10	80	4.6	5.2	.05
20	80	5.5	4.8	.05
45	80	7.1	4.8	.05
60	80	7.8	4.8	.05
120	80	12.6	4.1	.05
10	100	16.5	3.48	.05
20	100	30.0	3.16	.05
45	100	36.0	2.72	.05
60	100	38.0	2.32	.05
120	100	53.0	2.88	.06
5	120	37.0	3.14	.05
10	120	46.0	3.08	.06
20	120	55.0	2.68	.07
45	120	78.0	2.48	.11
60	120	89.0	2.46	.15
5	140	32.5	2.96	.07
10	140	42.0	3.10	.07
20	140	59.0	2.44	.26

When the control coating which did not contain a desensitizer was heated as described in Table D, it exhibited extremely high fog. The data in Table D above illustrates the desirability of utilizing temperatures of at least about 100° C. in resensitizing photographic emulsions to the formation of latent images in accordance with the invention. The elevated temperatures utilized in the process of the invention facilitate rapid resensitization of the emulsions' ability to record latent images so that they can be utilized in high-speed recording systems. Compounds 1 to 4 and 6 to 17 above give similar results when substituted for Compound 5.

EXAMPLE 4

Several samples of gold and sulfur sensitized negative-type, developing out gelatino-silver chlorobromide emulsions containing either 0, 0.3, 1.0 or 3.0 grams of the desensitizer, 4-nitro-6-chlorobenzotriazole (Compound 5) per mole of silver halide, were coated on 4 mil thick polyethylene terephthalate film bases at a coverage of 300 mg. of silver per square foot. The preapared films were exposed through a step wedge for one hour to a General Electric 3 watt, 6 volt projection bulb at a distance of approximately 10 feet and then developed in Developer B described above for 5 minutes and fixed with hypo in the usual manner. The control film sample containing no desensitizer was fully exposed while the film samples containing the desensitizer were completely blank giving a sensitivity difference greater than 1000 times. The desensitized film samples are resensitized to the formation of latent images by substantially greater than 10 times their desensitized or latent image inhibited speed level by heating the emulsions of the films with a platen at 140° C. for about 10 seconds.

EXAMPLE 5

A fine grain gelatino-silver chlorobromide emulsion containing 1.0 gram of the desensitizer, 4-nitro-6-chlorobenzotriazole (Compound 5), coated on glossy single-weight baryta-coated paper stock at a coverage of 475 mg. of silver per square foot was utilized to reproduce an image. An original comprising "carbon" copy paper stock containing an infrared absorbing image (printed matter on the paper) and non-image areas nonabsorptive of infrared was placed in contact with the prepared latent image inhibited photographic element. The resulting bipack was then exposed through the original to infrared radiation for a time sufficient to selectively resensitize the silver halide emulsion in the area beneath the infrared absorptive portions of the original. Reference is made to Miller, U.S. Patent No. 2,740,896, for suitable infrared exposing means. The original was removed and the selectively resensitized emulsion was exposed to white light to produce a latent image therein. The resulting infrared-treated and white light-exposed photographic element was then developed in Developer A as described in Example 1 and fixed in hypo in the usual manner to produce a correct-reading, direct-positive print on the film base. Compounds 1 to 4 and 6 to 17 above give similar results when substituted for Compound 5 as the desensitizer.

EXAMPLE 6

An emulsion of the type described in Example 1 was coated with 1.0 grams of the desensitizer 4-nitro-6-chlorobenzotriazole (Compound 5) per mole of silver halide. Samples of the dried coating were then thermally resensitized to the recording of latent images as described in Example 1 and exposed in an intensity scale sensitometer to record a latent image. The exposed strips were then further treated as described below before processing as described in Example 1:

(1) One of the strips was swabbed with a water-methyl alcohol solution before processing. It was found that this strip processed in a normal manner.

(2) Another of the strips was swabbed with a water-methyl alcohol solution and then stored in a dark room for one hour at room temperature before it was processed. It was found that this strip also processed in a normal manner.

(3) A third strip was swabbed as above and was then exposed to North Skylight for one hour. It was then processed to reveal that the original exposure had been substantially removed from the coating.

(4) A fourth strip was exposed directly to North Skylight without the swabbing step. It was found, after processing, that this strip had fogged completely to its maximum density.

Further experiments have exhibited the fact that after the moisturizing swabbing treatment of the emulsion containing 1 gram of the desensitizer per mole of silver halide, an additional light exposure, e.g., North Skylight, "erases" the latent image present thereon. The results discussed above, show that thermal resensitization in combination with the Herschel effect deems it possible to "erase" a recorded latent image and thereby use the light sensitive element again at some later date. Such results illustrate that the latent image can be kept for a designated time interval and if no situation occurs requiring the latent image to be developed, the latent image can be "erased" and the light sensitive element can then be reused for latent image storage.

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 as described hereinabove and as defined in the appended claims.

We claim:

1. A method of producing thermographic copies of an original containing portions highly absorptive of infrared radiation and portions substantially nonabsorptive of infrared radiation which comprises placing said original in surface contact with a desensitized photographic negative-type, developing out, unfogged, silver halide emulsion coated on a support, said densensitized emulsion containing sufficient quantity of a photographic silver halide emulsion chemical desensitizer selected from the group consisting of a mercury salt, a rhodium salt, an anthraquinone dye containing a sulfoalkylaminosulfone radical, a non-heterocyclic aromatic compound containing at least one nitro radical, and a heterocyclic compound contain-

ing at least one hetero atom selected from the group consisting of a sulfur atom and a nitrogen atom to render said emulsion substantially insensitive to the formation of latent images at radiations of wave lengths between about 1 and 1200 mμ, subjecting said emulsion through said original to infrared radiation to selectively heat to a temperature of about 100° C. to 300° C. and resensitize said emulsion to at least 10 times the desensitized speed to radiations of wave lengths between about 1 and 1200 mμ and to form a sensitized pattern portion in said emulsion corresponding to the said highly infrared absorptive portions of said original, fogging said sensitized pattern portion of said emulsion to form a latent image, and developing a silver image in said emulsion by treating said emulsion with a photographic developer.

2. A method of producing thermographic copies of an original containing portions highly absorptive of infrared radiation and portions substantially nonabsorptive of infrared radiation which comprises placing said original in surface contact with a densensitized photographic negative-type, developing out, unfogged, gold and sulfur sensitized gelatino-silver halide emulsion coated on a support, said emulsion being inhibited to the formation of latent images by incorporation therein of about .01 to 5 grams per mole of silver halide of a densensitizing agent selected from the group consisting of mercuric chloride, triammonium hexachlororhodite, 3,5-dinitrobenzhydrazide, 5-nitrobenzo - 1,2,3-triazole, 4-nitro-6-chlorobenzotriazole, 2,3 - dimethyl-6-nitrobenzothiazolium p-toluenesulfonate, 2-phenylbenzo-1,2,3-thiadiazolium bromide, N,N'-decamethylene - bis(quinoxalinium)perchlorate, Methylene blue chloride, 1-methyl-2-(p-nitrostyryl)-6-ethoxyquinolinium p-toluenesulfonate, 2 - (p-diethylaminophenyliminomethyl)-1,6-dimethylquinolinium chloride, 2-(p-dimethylaminophenyliminomethyl) - 3-ethylbenzothiazolium ethosulfate, phenosafranine chloride, pinakryptol green chloride, 1,3-diamino-5-methylphenazinium chloride, 3 - methyl-2-bis(phenylazo)methylene benzothiazoline, and anthraquinone-2-sulphotauride to render said emulsion substantially insensitive to the formation of latent images at radiations of wave lengths between about 1 and 1200 mμ, subjecting said emulsion through said original to infrared radiation to selectively heat to a temperature of about 100° C. to 300° C. and resensitize said emulsion to at least 10 times the densensitized speed to radiations of wave lengths between about 1 and 1200 mμ and to form a sensitized pattern portion in said emulsion corresponding to the said highly infrared absorptive portions of said original, fogging said sensitized pattern portion of said emulsion to form a latent image, and developing a silver image in said emulsion by treating said emulsion with a photographic developer.

3. A process for resensitizing a photographic element to the recording of latent images comprising a support, and coated on said support, a photographic negative type, developing-out, unfogged, silver halide emulsion which has been rendered substantially insensitive to the recording of latent images at radiations of wave lengths between about 1 and 1200 mμ by incorporation therein of a photographic silver halide emulsion chemical desensitizing agent selected from the group consisting of a mercury salt, rhodium salt, an anthraquinone dye containing a sulfoalkylaminosulfone radical, a nonheterocyclic aromatic compound containing at least one nitro radical, and a heterocyclic compound containing at least one hetero atom selected from the group consisting of a sulfur atom and a nitrogen atom, which comprises heating said emulsion to a temperature of about 100° C. to 300° C. for a period sufficient to resensitize said emulsion to at least 10 times the desensitized speed to radiations of wave lengths between about 1 and 1200 mμ.

4. A process for resensitizing a photographic element to the recording of latent images comprising a support, and coated on said support, a photographic negative-type, developing out, unfogged silver halide emulsion which has been rendered substantially insensitive to the recording of latent images at radiations of wave lengths between about 1 and 1200 mμ by incorporation therein of a photographic silver halide emulsion desensitizing heterocyclic compound with at least one hetero atom selected from the group consisting of a nitrogen atom and a sulfur atom and containing at least one benzene ring, which comprises heating said emulsion to a temperature of about 100° C. to 300° C. for a period sufficient to resensitize said emulsion to at least 10 times the desensitized speed to radiations of wave lengths between about 1 and 1200 mμ.

5. A process for resensitizing a photographic element to the recording of latent images comprising a support, and coated on said support, a photographic negative-type, developing out, unfogged, silver halide emulsion which has been rendered substantially insensitive to the formation of latent images at radiations of wavelengths between about 1 and 1200 mμ by incorporation therein of a photographic silver halide emulsion desensitizing nonheterocyclic aromatic compound containing at least one nitro radical, which comprises heating said emulsion to a temperature of about 100° C. to 300° C. for a period sufficient to resensitize said emulsion to at least 10 times the desensitized speed to radiations of wavelengths between about 1 and 1200 mμ.

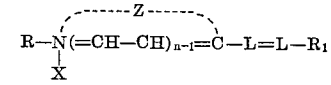
6. A process for resensitizing a photographic element to the recording of latent images comprising a support, and coated on said support, a photographic negative-type, developing out, unfogged silver halide emulsion which has been rendered substantially insensitive to the formation of latent images at radiations of wave lengths between about 1 and 1200 mμ by incorporation therein of a photographic silver halide emulsion desensitizing heavy metal salt selected from the group consisting of mercury and rhodium salts, which comprises heating said emulsion to a temperature of about 100° C. to 300° C. for a period sufficient to resensitize said emulsion to at least 10 times the desensitized speed to radiations of wave lengths between about 1 and 1200 mμ.

7. A process for resensitizing a photographic element to the recording of latent images comprising a support, and coated on said support, a photographic negative-type, developing out, unfogged silver halide emulsion which has been rendered substantially insensitive to the formation of latent images at radiations of wave lengths between about 1 and 1200 mμ by incorporation therein of a photographic silver halide emulsion desensitizing anthraquinone dye containing a sulfoalkylaminosulfone radical, which comprises heating said emulsion to a temperature of about 100° C. to 300° C. for a period sufficient to resensitize said emulsion to at least 10 times the desensitized speed to radiations of wave lengths between about 1 and 1200 mμ.

8. A process for resensitizing a photographic element to the recording of latent images comprising a support, and coated on said support, a photographic negative-type, developing out, unfogged silver halide emulsion which has been rendered substantially insensitive to radiations of wave lengths between about 1 and 1200 mμ by incorporation therein of a photographic silver halide emulsion desensitizing safranine dye, which comprises heating said emulsion to a temperature of about 100° C. to 300° C. for a period sufficient to resensitize said emulsion to at least 10 times the desensitized speed to radiations of wave lengths between about 1 and 1200 mμ.

9. A process for resensitizing a photographic element to the formation of latent images comprising a support, and coated on said support, a photographic negative-type, developing out, unfogged, silver halide emulsion which has been rendered substantially insensitive to the formation of latent images at radiations of wave lengths between about 1 and 1200 mμ by incorporation therein of

a photographic silver halide emulsion desensitizing cyclammonium quaternary salt having the formula



wherein:

(a) R is an alkyl radical,
(b) R_1 is an aryl radical,
(c) L is a methine radical,
(d) X is an acid radical,
(e) *n* is an integer of 1 to 2, and
(f) Z represents the necessary atoms to complete a heterocyclic ring containing 5 to 6 atoms and including at least one atom selected from the group consisting of sulfur atoms and nitrogen atoms,

which comprises heating said emulsion to a temperature of about 100° C. to 300° C. for a period sufficient to resensitize said emulsion to at least 10 times the desensitized speed to radiations of wave lengths between about 1 and 1200 mμ.

10. A method of resensitizing a photographic element to the recording of latent images comprising a relatively thin support, and coated on said support, a photographic negative-type, developing out, unfogged, silver halide emulsion which has been rendered substantially insensitive to the formation of latent images at radiations between about 1 and 1200 mμ by the incorporation therein of a photographic silver halide emulsion desensitizer selected from the class consisting of a mercury salt, a rhodium salt, an anthraquinone dye containing a sulfoalkylaminosulfone radical, a nonheterocyclic aromatic compound containing at least one nitro radical, and a heterocyclic compound containing at least one hetero atom selected from the group consisting of a sulfur atom and a nitrogen atom, which comprises contacting said photographic element with a heated surface and heating said emulsion to a temperature of about 100° C. to 300° C. for a period sufficient to restore the sensitivity to the recording of latent images of said emulsion to visible radiation substantially to the level prior to incorporation of said desensitizer.

11. A method for resensitizing a photographic element to the recording of latent images comprising a support, and coated on said support, a photographic negative-type, developing out, unfogged, gold and sulfur sensitized gelatino-silver halide emulsion which has been rendered substantially insensitive to the formation of latent images at radiations of wave lengths between about 1 and 1200 mμ by incorporation therein of about .01 to 5 grams per mole of silver halide of a desensitizing agent selected from the group consisting of mercuric chloride, triammonium hexachlororhodite, 3,5-dinitrobenzhydrazide, 5-nitrobenzo-1,2,3-triazole, 4-nitro-6-chlorobenzotriazole,2,-3-dimethyl-6-nitrobenzothiazolium p-toluenesulfonate, 2-phenylbenzo-1,2,3-thiadiazolium bromide, N,N'-decamethylene - bis(quinoxalinium)perchlorate, Methylene blue chloride, 1-methyl-2-(p-nitrostyryl)-6-ethoxyquinolinium p-toluenesulfonate, 2 - (p-diethylaminophenyliminomethyl)-1,6-dimethylquinolinium chloride, 2-(p-dimethylaminophenyliminomethyl)-3-ethylbenzothiazolium ethosulfate, phenosafranine chloride, pinakryptol green chloride, 1,3-diamino-5-methylphenazinium chloride, 3-methyl-2-bis(phenylazo)methylene benzothiazoline, and anthraquinone-2-sulphotauride, which comprises heating said emulsion to a temperature of about 100° C. to 300° C. for a period sufficient to resensitize said emulsion to at least 10 times the desensitized speed to radiations of wave lengths between about 1 and 1200 mμ.

12. A process as described in claim **3** wherein the photographic silver halide emulsion is supported on a photographic support about 1 to 10 mils in thickness and is selected from the group consisting of paper and polyester resin.

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