

# UNITED STATES PATENT OFFICE

2,541,472

## DIRECT POSITIVE EMULSION CONTAINING DESENSITIZING DYE

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This invention relates to photographic emulsions, and particularly to a direct positive photographic emulsion containing desensitizing dyes or compounds.

It is known that if a photographic silver halide emulsion which has been exposed to blue light is subsequently exposed to long-wave radiation before it is developed, some of the effect of the original exposure is destroyed. This is known as the Herschel effect. It is also known that desensitizing dyes may be added to the emulsion to increase reversal speed (Mees, *The Theory of the Photographic Process*, 1942, pages 280-282). The experiments described in the literature in which desensitizing dyes were used, were made with silver bromide emulsions, and reversal was found to be dependent upon absorption of light by the dye adsorbed to the silver bromide grains.

In these prior processes, reversal was not complete, that is, the reversal density was not reduced to zero. For this reason, the contrast of the image was low, and the background density high. With such processes it was impossible to obtain pure whites.

It is therefore an object of the present invention to provide a novel direct positive photographic process. A further object is to provide a direct positive emulsion in which high contrast images can be obtained. A still further object is to provide a method of producing direct positive images of low minimum density.

These objects are accomplished according to our invention by incorporating any of certain desensitizing compounds in a silver chloride emulsion, and fogging the emulsion before image-forming exposure.

The photographic emulsion used in our process is a silver chloride emulsion containing substantially no silver bromide or silver iodide. To this emulsion we add the desensitizing compound in amounts ranging from 0.1 gram to 2 grams of compound per 100 grams of silver chloride. The emulsion is then coated on a support and flashed with white light to fog it. It is then exposed to an image through a yellow filter and developed in the usual way to produce a positive image. The reversal speed of the emulsion is approximately  $\frac{1}{400}$  that of ordinary contact printing paper.

The desensitizing compounds used according to our invention are benzothiazole, quinoline, indolenine, benzotriazole, and rhodanine com-

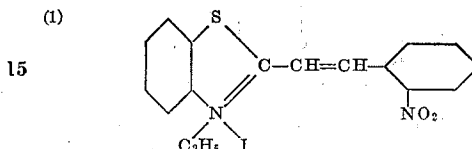
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pounds having one or more nitro groups attached to a benzene nucleus which is either a part of the heterocyclic compound or is attached to it through a doubly-bonded carbon to carbon chain.

5 The quaternary salts of the benzothiazole, quinoline and indolenine compounds are also suitable. Similar compounds without the nitro group showed no appreciable enhancement of the Herschel effect.

10 Compounds suitable for use according to our invention are the following:

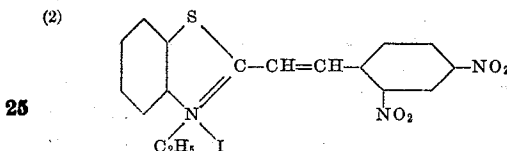
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2-(o-nitrostyryl)-3-ethylbenzothiazolium iodide. Also m- and p-nitrostyryl compounds

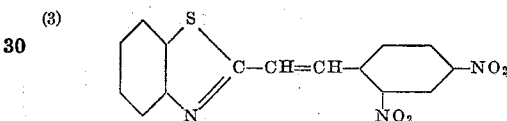
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2-(o,p-dinitrostyryl)-3-ethylbenzothiazolium iodide

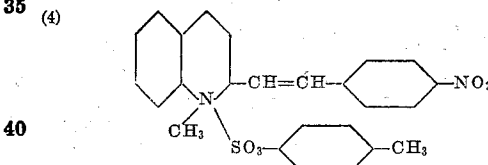
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2-(o,p-dinitrostyryl)-benzothiazole

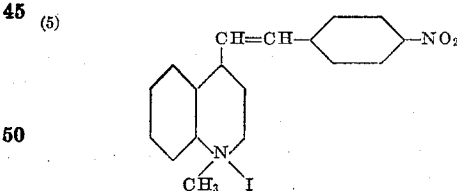
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2-(p-nitrostyryl)-quinoline metho-p-toluenesulfonate. Also 6-ethoxy derivative, and o- and m-nitrostyryl compounds

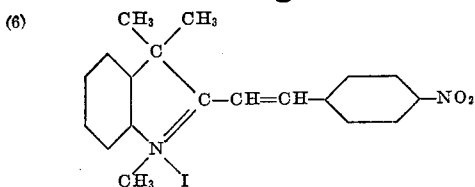
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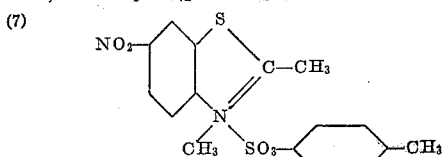
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4-(p-nitrostyryl)-quinoline methiodide

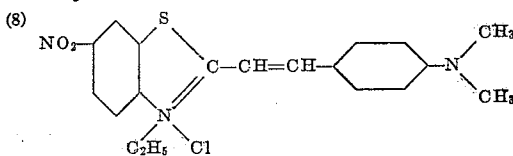
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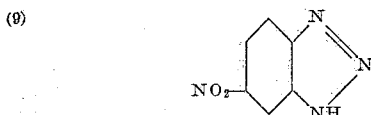
3,3-dimethyl-2-(p-nitrostyryl)-indolenine methiodide



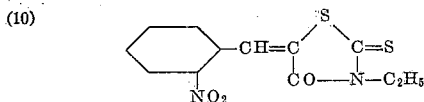
2-methyl-6-nitro-benzothiazole metho-p-toluene sulfonate



2-(p-dimethylaminostyryl)-3-ethyl-6-nitro-benzothiazolium chloride



6-nitro-benzo-1,2,3-triazole. Also 4-chloro- and 5-chloro-derivatives



5-o-nitrobenzylidene-3-ethyl-rhodanine

After incorporation of the nitro compound in the emulsion, the emulsion is coated on the support, which may be of paper, glass, synthetic resin, or other suitable material. The emulsion is then flashed to a high density with white light. The flash exposure should be of sufficient intensity to produce a high density upon development, although not necessarily the maximum density which the emulsion is capable of producing. A very heavy flash exposure requires a longer exposure to yellow light to remove its effect.

The emulsion may also be fogged chemically rather than by light, and in this case the fogging may be done before or after addition of the reversing compound using non-sulfide fogging reagents. Addition of formaldehyde to the emulsion is a suitable way of fogging the emulsion chemically. In this case no flash exposure is needed, and the only exposure necessary to give a positive image directly is the image-forming exposure through the yellow filter.

The reversal exposure is made with minus blue light, that is, light of 500 to 700 m $\mu$  wavelength. A No. 12 or No. 15 filter (Wratten Light Filters, Eastman Kodak Co., 1945) may be used over the light source to produce reversing light, or even a No. 2A filter if the blue speed of the emulsion is sufficiently low. Maximum reversal is obtained at 520 to 540 m $\mu$  wavelength.

Our invention will be illustrated by the following specific examples.

#### Example 1

This example illustrates fogging by light after addition of the reversing compound.

To 9.0 pounds of silver chloride emulsion con-

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taining an equivalent of 100 grams of silver nitrate was added 0.017 gram of 2-(p-nitrostyryl)-6-ethoxy-quinoline metho-p-toluene sulfonate. The emulsion was then coated on a non-glossy paper support and was then flashed with white light sufficient to give a density of 1.2 when developed in the following developer, diluted 1 part to 2 parts of water:

5	N-methyl-p-aminophenol sulfate	grams	3.1
10	Sodium sulfite, des.	do	45
	Hydroquinone	do	12
	Sodium carbonate, des.	do	67.5
	Potassium bromide	do	1.9
15	Water to	liter	1

The preflashed material can be exposed to an image with light modulated by a Wratten No. 15 filter.

#### Example 2

This example illustrates chemical fogging before addition of the reversing compound.

Seven lbs. of a silver chloride emulsion containing the equivalent of 100 g. of silver nitrate was heated to 40° C. and the pH adjusted to 7.8. Eight cc. of full strength (40%) formalin solution were added and the emulsion held for 10 minutes. At the end of the holding period the pH was adjusted to 6.0 and 0.125 g. of 2-(p-nitrostyryl)-quinoline metho-p-toluene sulfonate was added. The emulsion was then coated on a support.

The emulsions made according to our invention produce a low minimum density and a high maximum density on reversal. They are especially useful for reproduction of documents, letters and drawings.

It will be understood that the examples and modifications included herein are illustrative only.

We claim:

1. A direct positive photographic emulsion comprising a strongly fogged silver chloride emulsion containing a compound selected from the class consisting of benzothiazole, quinoline, indolenine, benzotriazole and rhodanine compounds and their alkyl quaternary salts having at least one nitro group attached to a benzene nucleus.

2. A direct positive photographic emulsion comprising a strongly fogged silver chloride emulsion containing a 2-nitrostyryl benzothiazole quaternary salt.

3. A direct positive photographic emulsion comprising a strongly fogged silver chloride emulsion containing a 2-(o-nitrostyryl)-3-ethylbenzothiazolium iodide).

4. A direct positive photographic emulsion comprising a strongly fogged silver chloride emulsion containing a 2-nitrostyryl quinoline quaternary salt.

5. A direct positive photographic emulsion comprising a strongly fogged silver chloride emulsion containing 2-(p-nitrostyryl) quinoline metho-p-toluene sulfonate.

6. A direct positive photographic emulsion comprising a strongly fogged silver chloride emulsion containing a 6-nitro-1,2,3-benzotriazole.

7. The method of making a direct positive photographic emulsion which comprises precipitating silver chloride in gelatin, adding to the emulsion a compound selected from the class consisting of benzothiazole, quinoline, indolenine, benzotriazole and rhodanine compounds and their alkyl quaternary salts having at least one nitro group attached to a benzene nucleus and strongly

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fogging the emulsion in the presence of said compound.

8. The method of making a direct positive photographic emulsion which comprises precipitating silver chloride in gelatin, chemically strongly fogging the emulsion and then adding to it a compound selected from the class consisting of benzothiazole, quinoline, indolenine, benzotriazole and rhodanine compounds and their alkyl quaternary salts having at least one nitro group attached to a benzene nucleus.

9. The method of making a direct positive photographic emulsion which comprises precipitating silver chloride in gelatin, chemically strongly fogging the emulsion and adding to the fogged emulsion of 2-nitrostyrylbenzothiazole quaternary salt.

10. The method of making a direct positive photographic emulsion which comprises precipitating silver chloride in gelatin, chemically strongly fogging the emulsion and adding to the fogged emulsion 2-(o-nitrostyryl)-3-ethylbenzothiazolium iodide.

11. The method of making a direct positive photographic emulsion which comprises precipitating silver chloride in gelatin, chemically strongly fogging the emulsion and adding to the fogged emulsion a 2-nitrostyryl quinoline quaternary salt.

12. The method of making a direct positive photographic emulsion which comprises precipi-

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tating silver chloride in gelatin, chemically strongly fogging the emulsion and adding to the fogged emulsion 2-(p-nitrostyryl) quinoline metho-p-toluene sulfonate.

13. The method of making a direct positive photographic emulsion which comprises precipitating silver chloride in gelatin, chemically strongly fogging the emulsion and adding to the fogged emulsion of 6-nitro benzotriazole.

14. The method of making a direct positive photographic emulsion which comprises precipitating silver chloride in gelatin, adjusting the emulsion to an alkaline condition, strongly fogging said emulsion chemically with formaldehyde, adjusting the emulsion to an acid condition and mixing with it a 2-nitrostyryl benzothiazole quaternary salt.

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