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3,157,507

OPTICAL SENSITIZATION OF PHOTOGRAPHIC MATERIALS SUITABLE FOR THE SILVER-DYE BLEACHING PROCESS

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1 Claim. (Cl. 96—99)

This invention provides a process for the optical sensitization of light-sensitive photographic layers that contain an azo-dyestuff and are suitable for the silver-dye bleaching process.

It is known that single color or multi-color photographic (pictures) images can be produced by the silver-dye bleaching process which depends on the destruction of dyestuff in accordance with the characteristics of the image. In that process an image is first recorded as a silver image by exposure and development by a normal photographic method in a light-sensitive layer uniformly colored with a dyestuff, and then the dyestuff present in the layer is locally destroyed by means of a silver-dye bleaching bath in proportion to the quantity of silver present locally. The silver is then removed to leave a dyestuff image that is the reverse of the original silver image. As in the case of color development processes that use multi-layer photographic materials, so also in the silver-dye bleaching process it is known to be of advantage to use for producing multi-color photographs a multi-layer material generally having three separate partial component color layers, of which the sensitivity is limited to different regions of the spectrum. A suitable multi-layer material contains, for example, on the support the red-sensitized layer containing the cyan dyestuff, upon that layer a green-sensitized layer containing a magenta dyestuff upon the latter layer a yellow filter layer to eliminate the action of the natural sensitivity of the layers beneath the filter layer, and as the uppermost layer a non-sensitized layer containing a yellow dyestuff.

In the silver-dye bleaching process an increase in the sensitivities of the several layers is especially important, because the light-sensitive silver halide layers each contain a dyestuff at the time of exposure, which dyestuff reduces the effective sensitivity of the layer by absorbing the exposure light. Such dyestuff-containing layers are very difficult to sensitize owing to the fact that the dyestuffs in the layers have a strong desensitizing action on the emulsion in addition to the aforesaid reduction in sensitivity due to absorption.

In the process of this invention photographic layers suitable for use in the silver-dye bleaching process and having unexpectedly high sensitivities are produced by incorporating as a sensitizer in a silver salt emulsion containing an azo-dyestuff a styryl or advantageously a cyanine dyestuff having a betaine-like structure. In such betaine-like dyestuffs the anion is present in the dyestuff molecule, and is thus bound by homopolar union to the N-alkyl radical of the dyestuff. They are therefore zwitter ions or internal salts. As such cyanine dyestuffs of betaine-like structure there are advantageously used carboxy-betaine-cyanines, sulfo-betaine-cyanines, or sulfate-

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betaine-cyanines, which may contain acid groups in addition to the aforesaid anion. There may also be used the corresponding styryl dyestuffs, i.e. carboxy-betaine-styryl, sulfo-betaine-styryl or sulfate-betaine-styryl dyestuffs.

Betaine-like dyestuffs of the above kind are known, see, for example, the disclosure of K. Mayer in "Zeitschrift für wissenschaftliche Photographie," vol. 52 (1958), part 7-9, pages 170-179. They have been used as sensitizers in gelatine emulsions containing color couplers. These emulsions were used for the production of photographic color images by color development. In such emulsions these betaine-like sensitizers are distinguished by the fact that their sensitizing action is not or is inappreciably changed by the presence of the color coupler. Nevertheless, it could not have been foreseen that such betaine-like sensitizers could be successfully used in emulsion layers containing azo-dyestuffs and suitable for the silver-dye bleaching process. Thus, it is known that azo-dyestuffs are generally more substantive in dyeing than are the colorless components used as couplers. This is especially true of polyazo-dyestuffs (to which belong substantially all cyan azo-dyestuffs), which, owing to their high substantivity, have a strong tendency to displace sensitizers in the silver halide surface and so reduce the sensitivity. It would, therefore, be expected that, in the case of layers containing azo-dyestuffs, the adsorption of sensitizer on to the silver halide, which adsorption is essential for the sensitizing action, would be impaired or prevented by the strong tendency of the azo-dyestuff to be taken up substantively. Accordingly, it might have been considered that the azo-dyestuff would displace the sensitizer adsorbed on the silver halide or that the dyestuff would form an inactive compound with the sensitizer. It could certainly not have been expected that the use of betaine-like sensitizers in accordance with this invention would result in the very great improvement in sensitivity which is in fact obtained.

It was also known that azo-dyestuffs possess an oxidizing action and are therefore essentially desensitizers, and that they reduce the sensitivity attainable with ordinary cyanine dyestuffs.

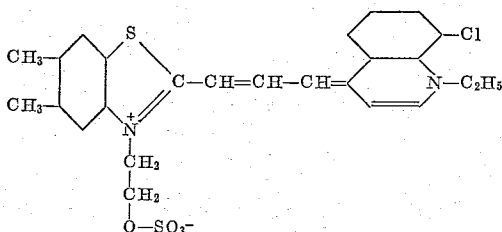
The high sensitivities attainable in accordance with the invention are also attained in layers containing azo-dyestuffs which are fixed by precipitation with basic precipitants, for example, biguanides. This is unexpected, because it is known that these basic precipitants (biguanide) possess a desensitizing action, and that therefore their presence in the emulsion would have been regarded as unfavorable to sensitization.

Essentially good results are also obtained with the use of azo-dyestuffs which contain phenol groups. It has been known for a long time that azo-dyestuffs containing phenol groups have a harmful effect on the action of known sensitizers, probably on account of the property of hydroxy-azo-dyestuffs existing in tautomeric form as hydrazones.

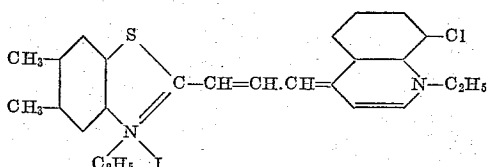
The method of sensitization in accordance with this invention is independent of the nature of the silver halide used. Furthermore, there may be used as layer formers, in addition to the usual gelatine, other layer-forming colloids. The invention is not limited to the production of multi-layer material, and also applies to making emul-

The following examples illustrate the invention:

100 grams of a silver bromide emulsion were sensitized for the long wavelength region of the spectrum with 1.0 milligram of a dyestuff having a betaine-like structure and of the formula



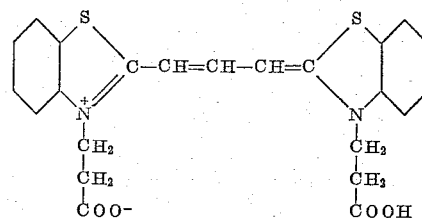
For the purpose of comparison 100 grams of a silver bromide emulsion were sensitized for the long wavelength region of the spectrum with 1.0 milligram of a dyestuff not having a betaine-like structure and of the formula



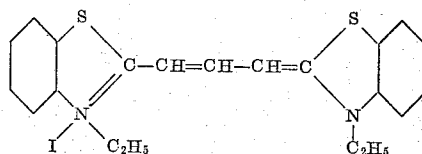
Sensitometric examination showed that the light sensitive material sensitized in accordance with the invention had a considerably higher sensitization than the corresponding control material.

	Relative sensitization (logarithmic values)	
	With blue light	With red light
Example 1.....	2.7	1.8
Control.....	2.1	0.6

200 grams of a silver bromide emulsion were sensitized for the region of the spectrum ranging from 500–700 $m\mu$ with 3 mgs. of a dyestuff having a betaine-like structure and of the formula



25 For the purpose of comparison 200 grams of a silver bromide emulsion were sensitized for the spectral region ranging from 500-700 $m\mu$ with 3.0 mgs., of a dyestuff having a non-betaine-like structure and of the formula

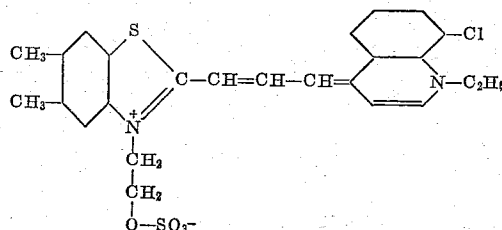


Sensitometric examination showed that the light-sensitive material prepared as described in the first paragraph of this example had a considerably higher sensitization than the control material.

50		Relative sensitization (logarithmic values)	
		With blue light	With red light
55	Paragraph 1 of Example 2	2.4	0.6
	Control	2.1	0.1

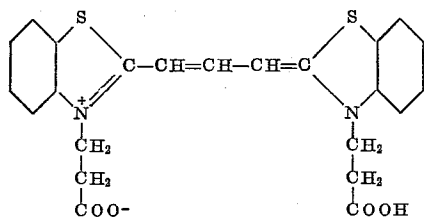
60 Photographic material having at least one light-sensitive silver halide emulsion layer containing an azo dyestuff containing phenolic hydroxyl groups and which is capable of being bleached out in the silver dye bleaching process and containing dyestuff selected from the group consisting of compounds of the formula

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and



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