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COLOR-PHOTOGRAPHIC BLEACH OUT DYESTUFF LAYERS

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7 Claims. (Cl. 95—7)

This invention relates to a method of producing color-photographic bleach-out dyestuff layers. Attempts to produce color photographic images by bleaching processes are very old, and innumerable variations of this process have been proposed. Very appreciable results have been obtained in this direction, but notwithstanding it has not been possible to make the finished images correspondingly durable. In particular there have been used for this purpose practically without exception basic dyestuffs. Reference is certainly contained in the literature to the effect that on occasion substantive or acid dyestuffs have also been investigated for the purpose in question, thus for example by Valenta in the Photographische Rundschau, 1911, page 56 etc.; but the results obtained were not of a useful kind, because the bleaching action was too slow. Indications have also been furnished from other sources, but these related in themselves to dyestuffs extremely unfast in light.

The surprising fact has been discovered that the bleaching, i. e. the light-sensitiveness of acid dyestuffs, which in themselves are lasting in light, may be very considerably increased if in addition to a desired sensitizer there is also introduced into the layer a suitable auxiliary body, which activates the sensitizer. As auxiliary body there are employed the acid salts of multi-base acids, organic or inorganic acids or acid or reducing substances, such as phenols or aminophenols, and more particularly those which are suitable as photographic developers. An extremely high sensitiveness to light is obtained, if a durable double compound of hypo-sulfurous acid is employed, for example sodium formaldehyde sulfo oxalate or its double metal salts. These compounds may be employed either alone as sensitizers or also admixed with other sensitizers. As additional auxiliary bodies there are employed metal salts having a catalytical action, for example vanadium or titanium salts. Inorganic sulfur compounds, such as sulfides or sulfites may be incorporated in the layer.

Example 1

Chloramine light-red 7BL is applied to ordinary paper or baryta paper with anethole as sensitizer and potassium bisulfate as auxiliary body. In sunlight a very vigorous bleaching ac-

tion is apparent after approximately 10 minutes, which action continues up to complete bleaching.

Example 2

Tartrazine is mixed with thiosinamine and sulfuric acid or thiocarbamide and sulfuric acid, either with gelatine as a binding agent or, as in Example 1, painted on to paper. Exposure is made in sunlight and the tartrazine is bleached to a pure white in approximately 5 minutes.

Suitable sensitizing solutions are, for example, as follows:

- A. 100 grammes water
5 grammes thiosinamine
25 grammes 20% sodium bisulfate solution

The sensitizing effect, which in itself is of a powerful kind, may be further increased by the addition of 1 gramme monomethyl paramidophenol sulfate.

- B. 200 grammes water
5 grammes rongalite
5 grammes thiocarbamide

There are employed for 4 ccm. gelatine 4%, approximately $\frac{1}{2}$ ccm. 1% dyestuff solution and $\frac{1}{2}$ ccm. sensitizer to 1 qdm.

Example 3

For a three-color image there are employed for example Tartrazine, Patent Blue A, Fast Red D in mixture with a colloid, for example gelatine, in conjunction with one of the sensitizers set forth above.

The process according to the invention reveals the particular advantage, that, as compared with the dyes hitherto in use, dyestuffs may be employed which are extremely fast in light, and after the fixing an additional bleaching of the dyestuff does not take place. The dyestuffs employed in accordance with the invention possess the advantage that the substantive dyestuffs remain adhering to the fibres of the paper, or single substantive dyestuffs and also the acid dyestuffs impregnate the gelatine in such fashion that the same cannot be washed out or only with extreme difficulty. The fixing of the bleached images is accordingly very simple. The images are washed subsequently in water, as a result of which the sensitizer is dissolved away and the

dyestuff remains adhering to the backing or support or in the binding agent (for example in the gelatine), and cannot be washed out or at least only with extreme difficulty. There may

5 also be performed subsequently a short after-treatment in copper sulfate or alum or in another mordant forming means for the purpose of increasing the fastness in light.

10 The dyestuffs may be employed in mixture or also poured in the known manner on to superimposed layers. For copying purposes there are employed either tripack images or other master images or color-screen images as desired.

15 It has been found that large-grain screen images may be copied particularly well, as in this case parallax errors and whitening of the colors are unable to occur.

Suitable dyestuffs are, for example, Diamine Pure Blue FF, Tartrazine, New Patent Blue, 20 Phloxine B B N, Xylene Light Green 6B, Patent Blue, Chromium Green GD extra, Guinea Blue, Fast Red D, Chloramine Light Red 7 BL, Chromium Fast Red BD paste, Geranine, Complementary Red D, Pinatype Blue D, Xylene Fast 25 Blue FF.

The index numbers of the dyes quoted in the foregoing examples are set forth in "Schultz Dyestuff Tables", Berlin, 5th Ed., 1920, as follows:—

30	Chloramine Light Red 7BL	No number found (manufactured by Sandor, Basel, Switzerland).
	Tartrazine 23	
	Patent Blue 545	
	Fast Red D 168	
35	Diamine Pure Blue FF 424	
	New Patent Blue 563	
	Phloxine 596	
	Chromium Fast Red BD	Schultz, page 379 (no number).
	Geranine 118	Do.
	Complementary Red	Mentioned in the "Pina Handbuch" of the I. G. Farbenindustrie A.-G.
40	Pinatype Blue	Do.
	Xylene Light Green 6B	No number (manufactured by Sandor, Basel).
	Xylene Fast Blue	Do.
	Chromium Green GD extra 509	
	Guinea Blue	

45 It will be understood that no restriction is made to the particular examples described in the above or to the specific samples quoted, and that numerous modifications and substitutions

are quite possible within the meaning of the above description and the annexed claims without departing from the spirit of the invention.

I claim:—

1. Photographic bleach-out layers comprising 5 a colloidal carrier fastly dyed by at least one acid azo-dyestuff and having incorporated in addition a sensitizer and an agent activating the said sensitizer, one at least of the additions being dischargeable. 10

2. Photographic bleach-out layers comprising a colloidal carrier fastly dyed by at least one acid azo-dyestuff and having incorporated in addition a sensitizer and a substance of acid reaction activating the said sensitizer, one at 15 least of the additions being dischargeable.

3. Photographic bleach-out layers comprising a colloidal carrier fastly dyed by at least one acid azo-dyestuff and having incorporated in addition a sensitizer and a reducing substance 20 activating the said sensitizer, one at least of the additions being dischargeable.

4. Photographic bleach-out layers comprising a colloidal carrier fastly dyed by at least one acid azo-dyestuff and having incorporated in 25 addition a compound of the thio-urea-group and an agent activating the said sensitizer, one at least of the additions being dischargeable.

5. Photographic bleach-out layers comprising a colloidal carrier fastly dyed by at least one 30 acid azo-dyestuff and having incorporated in addition an etheric oil and an agent activating the said sensitizer, one at least of the additions being dischargeable.

6. Photographic bleach-out layers comprising 35 a colloidal carrier fastly dyed by at least one acid azo-dyestuff and having incorporated in addition a double compound of hyposulfurous acid and an agent activating the said sensitizer, one at least of the additions being dischargeable. 40

7. Photographic bleach-out layers comprising a colloidal carrier fastly dyed by at least one acid azo-dyestuff and having incorporated in addition a compound of the thio-urea-group and a substance of acid reaction, one at least of the 45 additions being dischargeable.

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