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PROCESS FOR STABILIZING PRINTS OBTAINED BY PHOTOGRAPHIC BLEACHING

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1 Claim. (Cl. 95—7)

The present invention has for object various treatments of bleaching layers sensitized by thiocarbamic derivatives, in order to ensure or improve the stability of the prints obtained by photographic bleaching.

It is known that the methods proposed up to now for fixing the bleaching layers against the action of light nearly exclusively belong to the dyeing art, as mordanting by tanin, treatment with copper solutions, etc. The inconveniences of these methods consisted in the coloration of the light parts of the proofs printed, in the changing, sometimes fundamental, of the tints obtained and in the necessity of effecting long washings for eliminating the agent in excess.

It has also been proposed, especially for completing the treatments mentioned, to use baths of organic solvents, such as alcohol for eliminating the sensitizers. It has been proposed, for instance for basic dye-stuffs, to convert them into borofluoric derivatives and to eliminate the sensitizer by dissolution in a suitable solvent. It has been proposed to use powerful oxidising agents (nitrous acid) or powerful reducing agents (sulphurous acid) for destroying them. These processes allow of only incompletely attaining the result sought for and are sometimes prejudicial to the organic materials with which they are placed in contact, and particularly the substratum, the dye-stuffs and the support.

The present invention is based on the idea that an intimate contact is necessary between the dyestuffs and the sensitizers, for imparting to these dye-stuffs a good sensitiveness to light, and that the dissociation of the sensitizer and of the dyestuff, considerably diminish the sensitiveness to light of the dye-stuffs.

According to the invention, the layers are treated, after exposure to light, by one or more solutions having the property of precipitating the sensitizer. By precipitating the sensitizer a dissociation of the dyestuffs and sensitizers is obtained.

If need be, respectively according to the composition of the layer and according to the dyestuffs it contains, the precipitation of the sensitizer will be completed by one or both of the following accessory means:

1. Elimination of the sensitizer from the layer by washing,
2. Rendering the dyestuff, or respectively the dyestuffs insoluble.

The most simple method of carrying into practice this process consists in the fact that the layer, after exposure to light is introduced in an aqueous solution capable of completely precipitating the sensitizer. Use is made for instance of a solution of mercuric chloride as solution for precipitating the thiourea derivative. In the case of a highly soluble thiourea derivative, the elimination of the sensitizer from the layer takes place extremely rapidly, since, among other reasons, the concentration of the sensitizer in the bath is constantly practically null, owing to the precipitation. Another advantage in this case is that by choosing a suitable concentration of the mercury salt, the precipitate is only formed in the precipitating bath and not on the layer itself, as it is soluble in an excess of the thiourea derivative.

If the sensitizer is soluble in water, it will be generally, first of all, eliminated for the major part by washing in water, and alone the last traces of sensitizer, practically extraordinarily difficult to eliminate, will be precipitated in a suitable manner. The layer will be perfectly desensitized thereby, as an adsorption of the remaining portions of sensitizer on the dyestuff particles will no longer be possible.

Concerning the rendering of the dyestuff insoluble, this action can be obtained by the use of a suitable bath, if need be, even before eliminating the sensitizer by washing; the sensitizer can also be eliminated by washing in a bath having the faculty of precipitating dyestuffs; the dyestuffs can also be rendered insoluble beforehand, when manufacturing the sensitized layer; finally the dyestuff can be rendered insoluble in the very bath intended for precipitating the sensitizer. This latter result is obtained in case it is a question of basic dyestuffs, for instance, by the above mentioned bath, consisting in a solution of mercuric chloride. For instance, the Nile blue dyestuff (Schultz, VII, edition No. 1029) is, by means of this bath, instantaneously precipitated, fixed and maintained in the layer. For increasing the fastness of dyestuffs to washing, in case basic dyestuffs are under consideration, if acid dyestuffs and more especially azoic dyestuffs are contemplated, use can be made, for that purpose, of organic quaternary ammonium bases, also called cationactive substances, or use can be made for rendering the dyestuff insoluble, of soluble derivatives of tin, silicon, tungsten, and molybdenum. As mentioned use can be made for precipitating the sensitizer and rendering the dyestuffs insoluble, of a single solution, if need be, a solution of a plurality of products.

For eliminating the activity by precipitating the thiourea derivatives as sensitizers, the most suitable products are actually, mercury salts. Results are also obtained for instance with certain compound salts of tin and silicon.

These latter salts have the property of forming with an excess of thiocarbamic derivative or by means of any other sulphocarbamic derivative a complex salt, soluble in water, which can be used for eliminating from the layer a sulphocarbamic derivative insoluble in water. It is thus that diethylallylsulpho-urea is easily eliminated from a layer, which diethylallylsulpho-urea is completely insoluble in water, by means for instance of a mixture of sulpho-carbamide and mercuric chloride, these substances can also be incorporated beforehand, when manufacturing the sensitive layer.

A few examples of the process according to the invention will be given hereinafter, it being understood that said examples are not limiting.

Example 1.—The following solution is prepared: 200 grams of water, 30 grams of ammonium chlorostannate, 18 grams of silicotungstic acid. A paper bleaching print prepared with basic dyestuffs is treated in a bath of this solution, it is washed with water for 5 minutes, then it is dried. The stability to light of the print will thus correspond to the initial stability of the basic dyestuffs incorporated, and the tints to the initial colours.

Example 2.—A layer of the solution according to Example 1 is applied on an exposed bleaching out layer. It is dried. The layer is nearly completely desensitized, without changing the tints.

Example 3.—On an exposed bleaching out layer containing naphtionic red, oxalic acid and diethanolallylsulpho-urea, is spread a solution of m - diacetylamino - phenyl - trimethylammonium chloride, it is then washed for a few minutes. Perfect fastness to light is obtained.

Example 4.—After exposure a trichrome bleaching out layer is treated, containing as dyestuffs only basic dyestuffs and sulphocarbamic derivatives, as sensitizers, first of all in the following bath: 200 grams of water, 10 grams of mercuric chloride, 1 gram of concentrated hydrochloric acid. Then it is washed in the following bath: 1000 grams of water, 50 grams of sulphourea.

Example 5.—A bleaching out layer is prepared as follows: in 1000 grams of water are dissolved 25 grams of gelatine, 5 grams of hydrochloric acid, 4 grams of Nile blue sulphate, 6.5 grams of Flavindulin O, 3.5 grams of sulphopyronine G, 100 grams of acetamide and 30 grams of oxalic acid. Then, the mixture of 60 grams of diethylallylsulpho-urea and 25 grams of mercuric chloride which was previously heated with 50 grams of water, is added. It is spread on paper, exposed to light under a negative and the proof is washed for 15 minutes.

We claim:

Process for stabilizing prints obtained by photographic bleaching of layers containing bleaching dyestuffs and thiourea derivatives, consisting in eliminating, after exposure of the sensitized layer to light and elimination of the major portion of the thiourea derivative by washing with water, the intimate contact between the dyestuffs and remainder of the thiourea derivative, by precipitating the latter by means of mercuric salts incorporated with the layer when it is manufactured, which have remained soluble and have not formed a precipitate owing to the presence of an excess of thiourea derivative.

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