April 27, 1943. W. FERMAZIN 2,317,750

SYSTEM OF IMPROVING PHOTOGRAPHIC LAYERS

Filed Nov. 27, 1939

Fig. 1.

PRIOR ART.

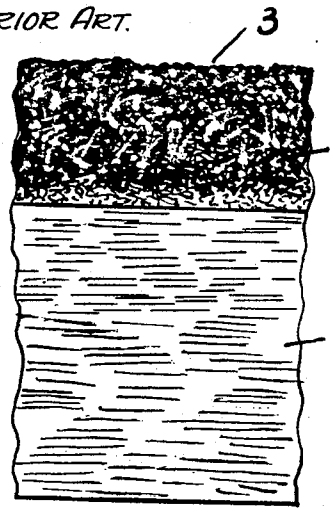


Fig. 2.

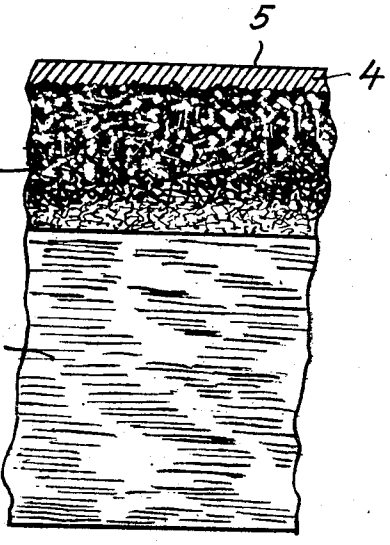
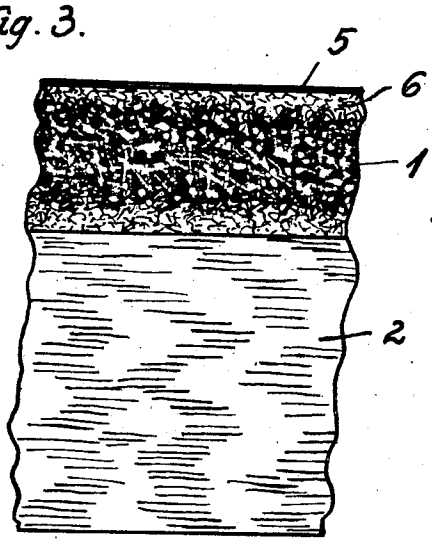


Fig. 3.



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Patented Apr. 27, 1943

2,317,750

UNITED STATES PATENT OFFICE

2,317,750

SYSTEM OF IMPROVING PHOTOGRAPHIC LAYERS

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Application November 27, 1939, Serial No. 306,272
In Germany August 11, 1939

3 Claims. (Cl. 95—88)

This invention relates to methods and treating baths for the improvement of photographic records or pictures.

It is an object of the present invention to improve the photographic pictures during the photographic treatment of the same in the photographic baths, for example, during the development and fixation, during the action of tanning and dyeing liquids, toning baths or the like.

Another object of the invention is to form a smooth surface layer on the rough surface of the image layer by solidified colloids, for avoiding any diffusion of light and for rendering the photographic image more brilliant.

Still another object of the invention is to provide a protective layer for the sensitive silver-containing gelatine layer which is present for instance on cinematographic films.

With these and further objects in view which will be apparent from the within disclosures the process according to the invention comprises introducing dispersed colloids into some of the baths following each other in the manufacturing process and coagulating the colloids adhering to the photographic layer in one or more of the subsequent baths, for example, by coagulating substances admixed thereto or by changing the pH value thereof, more particularly by different electrolytic polarity. Advantageously, the treating baths contain softening agents which preferably are not dissociated or gelatinizing agents for the gelatinizing colloids contained in the respective bath, for instance, in a developer.

According to a special feature of the invention, the colloids may be introduced into the baths together with the photographic layer, for example, the cinematographic film which is to be treated. The incorporation of the colloids into the photographic layers may be effected by further swelling said layers after the same have left the baths, by action of heat, to such an extent that the deposited colloidal layer penetrates entirely or partly into the porous photographic image layer, whereby the transparency is substantially increased due to elimination of the interior dispersion of light.

Hitherto, in order to improve cinematographic films and the like, the photographic layer has been subjected to a separate improving treatment after the photographic process. On the other hand if protective layers are applied on the photographic raw material in order to prevent the same from being damaged in the camera, which layers are not dissolved in the developer, the drawback occurs that in a contact printing process the two photographic layers which shall be in direct contact with each other are spaced by the protective layer whereby the sharpness of the print is reduced. This drawback would be still more considerable if photographic positive films and more particularly cinematographic films which are most liable to scratching, would be provided with a protective layer applied on the raw film, since the spacing in the printing process would be further increased thereby. Further drawbacks occur by the reflection produced by such protective layers. Moreover, the development process is retarded and rendered non-uniform unless the layer is of a uniform thickness and very homogeneous.

The said drawbacks of the existing methods are avoided by my novel method above pointed out. In case of layers of silver halides, both the developer and the fixing bath and in some instances also the intermediate or watering bath may contain the above mentioned colloids in the form of a dispersion. Advantageously, the colloids are admixed to the first or developing bath since the photographic layer when introduced into the bath in a dry state has the maximum enriching power due to the maximum capillary attraction and adsorptive swelling power existing in this state.

It is also contemplated within the purview of this invention to admix colloids which are soluble in acid to an acid fixing bath and causing the formation of gels in an intermediate bath, prior to the watering bath, by means of substances causing coagulation or basic reaction.

The invention will be better understood by reference to the drawing in which—

Fig. 1 is a section through a film developed in known manner.

Fig. 2 is a section through a film developed in accordance with the invention in a developing bath containing colloids.

Fig. 3 is a section through the film shown in Fig. 2, after a swelling treatment in a drying chamber.

In the figures, item 1 represents the photographic layer and item 2 is the support therefor of Celluloid or the like. As shown in Fig. 1, the known process results in a rough surface 3 of the photographic layer while in Fig. 2, a colloidal layer 4 is formed on the photographic layer 1 by the process according to the invention, thus forming a smooth surface 5. While the said colloidal layer is at first of a thickness which might cause the above mentioned disadvantages pro-

duced by protective layers on the photographic layer, Fig. 3 shows that the said colloidal layer is incorporated in the photographic layer 1 as indicated by the points 6, by the swelling treatment in the drying chamber, thus forming a smooth surface 5 without any substantial additional thickness of the photographic layer.

Where the photographic picture is produced by treatment in a toning or dye-stuff bath, the dispersed colloids may be admixed to the toning or dyeing bath while coagulating agents are admixed to the clarifying bath. Photographic layers containing dye-stuff producing agents in addition to silver-halide or dye-stuff liable to destruction or decomposition by the formation of metal in a reducing reaction may be treated in a similar manner. For example, if the photographic material treated in a developer as above described is acted upon by acidfied liquids (pH less than 6.5) such as, intermediate or fixing baths, a coagulating effect occurs with respect to the colloids and the dispersions solidify due to the swelling together of their boundaries, thus forming solid layers which are inseparably connected with, or anchored in, the photographic layer.

The colloids may be admixed to the chemical substances forming the developing, fixing and like baths. However, it is also possible as pointed out above, to introduce the colloids in the form of a layer applied to the exposed raw film for being intimately anchored in the image layers by coagulation.

Advantageously, softening agents or gelatinizing agents are admixed to the baths containing the colloids which agents act upon the protective layer already existing or formed in the baths as well as upon the image layer and if desired upon the colloids forming the support of the image layer. Such agents shall not be dissociated or only slightly dissociated in order to avoid interference with the developing process. In this respect, organic esters of the fatty acids are very suitable.

Example 1.—An embodiment of a developing bath in accordance with the invention. The film is developed in a developing bath comprising:

	Grams
Water	1000
Sulfate of monomethyl-para-amido-phenol	4
Hydrochinone	2
Sodium sulfite	80
Acid casein	10–30
Borax	8
Potassium bromide	0.25

The casein is used in the form of commercial pure acid casein which can be dispersed in water at pH=6.5 but is precipitated in the form of a free acid casein when approximating the isoelectric point pH=4.6

Example 2.—The film is developed in a developing bath comprising:

1000 grs. of an aqueous, slightly ammoniacal dispersion of polymerization products, e. g., of acryl- or methacryl-acid,
4 grs. sulfate of monoethyl-para-amido-phenol,
50 grs. sulfite of sodium,
2 grs. soda.

Example 3.—The film is fixed in a fixing bath solution acidified by acetic acid and containing dispersed gelatine. After the fixing and prior to the watering the film is immersed in an aqueous intermediate bath containing about 50 percent of a mixture of one part by weight of ammonia and one part by weight of alcohol.

Example 4.—The film is treated in a dyeing bath comprising a mixture of

	Per cent
Dyestuff	5
Gelatine	2
Hydrate of chloral in an aqueous solution	1

After the dyeing bath and prior to the clarifying bath the film is immersed in an aqueous bath containing 50% of a mixture of alcohol and acetone, for coagulation.

The baths according to the above examples are advantageously provided with 2.5–10% of softening agents which are soluble in water, such as, for example, lactic acid ethyl ester, glycerinated fatty acid ester or the like. The above percentages are by weight.

It will be understood that the invention is not restricted to the examples hereinbefore stated, but comprises any formation of a layer within the bath for the image production which is based on dispersion or coagulation of colloids by different properties of the baths.

The so-called hardening-fixing baths may now be used in a concentration acting sufficiently rapidly without interfering with the photographic image layer of layers. The drawbacks occurring usually with hardening baths, such as, to slowly growing resistivity against mechanical attacks or hornifying of the layer occurring very soon and brittleness thereby caused are avoided in this manner.

The treating baths and methods of the present invention have been described in detail with reference to specific embodiments. It is to be understood, however, that the invention is not limited by such specific reference but is broader in scope and capable of other embodiments than those specifically described and illustrated in the drawing.

I claim:

1. In the art of finishing photographic layers by subjecting the layers to a fixing bath and at least one further treating bath in succession, the steps of admixing to said fixing bath a dispersed colloid, and causing coagulation of said colloid in said further treating bath so as to produce a smooth protective surface upon the final layers by the solidified colloid.

2. In the art of finishing photographic layers by subjecting the layers to a dyeing bath and at least one further treating bath in succession, the steps of admixing to said dyeing bath a dispersed colloid and causing coagulation of said colloid in said further treating bath so as to produce a smooth protective surface upon the layers by the solidified colloid.

3. In the art of finishing photographic layers by subjecting the layers to different treating baths in succession, the steps of admixing to at least one of said treating baths a dispersed colloid, and causing coagulation of said colloid in at least one of the subsequent treating baths, thereafter heat treating the layers upon leaving said last bath to form a smooth protective layer by the solidified colloid upon and being at least partly incorporated in the final layers.

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