

UNITED STATES PATENT OFFICE

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PHOTOGRAPHIC GELATINE LAYER

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The present invention relates to an improvement in the manufacture of photographic materials and more particularly to a process of hardening the gelatinous emulsion layers on photographic films, plates or papers.

Another object of the invention are the new photographic materials provided with a gelatine layer prepared according to the invention.

It is known to harden gelatinous emulsion layers by means of formaline or acrolein. The layers thus hardened, however, show a very annoying afterhardening. The melting point of a silver halide gelatine emulsion hardened by means of formaline raises, for instance, from 35° C. to 72° C. after a two days' storage at 50° C.

According to this invention the afterhardening can considerably be reduced by using dialdehydes as hardening agents for photographic gelatine emulsions. The reaction of dialdehydes with the gelatine obviously occurs at a considerably higher speed. Thus, for instance, the melting point of a gelatine layer hardened by means of a dialdehyde raises, after a two days' storage at 50° C., only from 37° C. to 42° C., and even after a ten days' storage at this temperature it only raises to 49° C. Consequently, it is possible, when making use of the dialdehydes, to impart to the said gelatine layer a hardness that remains rather constant.

Moreover, the dialdehydes have, as compared with formaline and acrolein, the further advantage of exerting a stronger hardening action, when comparing equivalent quantities.

Also when compared with the metal salts, for instance of aluminium or chromium, known to be hardening agents for albuminous substances the dialdehydes involve an advantage inasmuch as the hardness obtained by their action remains constant in the alkaline developer and is not reduced, as it is the case with the said metal salts, by the action of the alkali.

Dialdehydes suitable according to this invention are, for instance, glyoxal and mesoxaldialdehyde. Both the monomeric and the

polymeric forms are suited, with the difference that the latter have a somewhat smaller hardening action. The hardening process may be carried out in the same way as with formaldehyde, either by adding the hardening agent to a solution of the gelatine or by subsequently bathing the shaped and dried albuminous bodies in a solution of the hardening agent.

The following examples illustrate the invention:

(1) 500 grams of a photographic gelatine emulsion containing 8-10 per cent. of gelatine, comprising a silver halide, and melting when dry at 32° C., are mixed at 35° C. with 4 cc. of a 1 per cent. aqueous solution of monomeric glyoxal or 5 cc. of a 1 per cent. solution of p-glyoxal and poured in the usual manner on glass plates or films. After drying the layer shows a melting point of 36° C.

(2) A glass plate coated with a gelatine silver halide emulsion layer melting at 32° C. is bathed for 2 minutes in a 1 per cent. aqueous solution of monomeric glyoxal. After drying the layer has a melting point exceeding 40° C.

In an analogous manner other photographic materials such as films or papers may be prepared. Instead of glyoxal mesoxaldialdehyde may be used or any other aliphatic dialdehyde showing an equivalent behaviour. A few simple comparative experiments should be made to determine the best kind of dialdehyde and the most suitable amount to employ with a particular gelatine which is to be hardened to a desired degree.

As well known a peculiar hardening of gelatinous layers is necessary when exporting photographic materials into the tropics.

What I claim is:

1. In the manufacture of photographic articles provided with a gelatine emulsion layer of constant hardness the step which comprises acting upon the said gelatine emulsion with a dilute solution of an aliphatic dialdehyde.

2. In the manufacture of photographic articles provided with a gelatine emulsion layer of constant hardness the step which

comprises acting upon the said gelatine emulsion with a dilute solution of glyoxal.

3. In the manufacture of photographic articles provided with a gelatine emulsion layer of constant hardness the step which comprises acting upon the said gelatine emulsion with a dilute solution of polymerized glyoxal.

4. In the manufacture of photographic articles provided with a gelatine emulsion layer of constant hardness the step which comprises acting upon the said gelatine emulsion with a dilute solution of mesoxaldialdehyde.

5. Photographic materials provided with a gelatine silver halide emulsion layer, said gelatine layer containing the condensation product of gelatine with an aliphatic dialdehyde.

6. Photographic materials provided with a gelatine silver halide emulsion layer, said gelatine layer containing the condensation product of gelatine with glyoxal.

7. Photographic materials provided with a gelatine silver halide emulsion layer, said gelatine layer containing the condensation product of gelatine with a polymerized glyoxal.

8. Photographic materials provided with a gelatine silver halide emulsion layer, said gelatine layer containing the condensation product of gelatine with mesoxaldialdehyde.

In testimony whereof, I affix my signature.

JOHANNES BRUNKEN.

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