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## PROCESS OF HARDENING PROTEIN SUBSTANCES

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The present invention relates to an improved process of hardening protein substances and more particularly to the hardening of photographic silver halide gelatin layers.

It is known practice to harden photographic silver halide emulsion layers by treatment with an aldehyde, and for this purpose formaldehyde has mainly been used. Other known hardening aldehydes are: glyoxal, dibromoacrolein, oxyaldehyde. By addition of these aldehydes to photographic emulsions, however, there is produced, particularly when a large proportion is used in order to obtain a high degree of hardening, a diminution of the threshold sensitivity.

It is an object of the present invention to provide a process of hardening protein substances and simultaneously increasing the threshold sensitivity, so that the disadvantage hitherto accompanying the use of a hardening agent is eliminated or minimized.

Another object of the invention is the provision of a process of hardening gelatin by means of aliphatic aldehyde carboxylic acids.

A further object of the invention is to provide a process of hardening a photographic gelatin layer and simultaneously increasing its threshold sensitivity by means of aliphatic aldehyde carboxylic acids which contain certain radicals.

Other objects are set forth in the following specification.

Examples of aldehyde carboxylic acids suitable for the invention are glyoxylic acid, glyoxyl-propionic acid, glyoxyl-isobutyric acid, formyl-acrylic acid, formyl-acetic acid, β-formyl-propionic acid, and γ-formyl-butyric acid. By substitution, especially by introduction of hydroxy-, keto- or amino-groups, there is moveover obtained a large number of new, valuable aldehyde carboxylic acids suitable for hardening. Halogen is not suitable as a substituent because it effects no or only a very slight increasing of the threshold sensitivity. By halogenated aldehyde carboxylic acids there is also obtained a flattening of the gradation.

The application of the new hardening agents follows the method usual in photographic practice. The hardening agents may be added to the washing emulsion shortly before the casting operation; they may also be added to the cast layer in the undeveloped or developed condition by treating the layer in a bath containing the substances. It is a matter of indifference on what kind of support the photographic silver halide emulsion is carried. It may be glass, paper, cellulose, cellulose derivative or metal. The application of the new hardening agent is not limited to the actual photographic silver halide emulsion; it may also be used to harden an under-layer or an over-layer or a backing layer, also intermediate layers and preparatory layers of gelatin or other protein bodies or mixtures of such with other colloids. The preparation of the mixture to be used varies somewhat according to the melting point desired. In general 50–5000 milligrams per kilo of a gelatin solution of about 10 per cent strength is desirable, but the invention is not limited to such preparation. Among other protein layers which can be hardened by the new agents may be named albumen, casein, and gliadine.

The following examples illustrate the invention:

*Example 1*

1 kilo of gelatin silver halide emulsion for negative purposes, having a gelatin content of about 8–9 per cent, and optically sensitized by means of a dyestuff, is mixed in molten condition with 200 milligrams of formylacrylic acid and then cast in the usual manner. The dry layer melts at 36° C., while the unhardened layer melts at 33° C. The increase of threshold sensitivity is about 75 per cent. In the course of storage the layer becomes somewhat harder.

*Example 2*

1 kilo of a silver halide emulsion containing 8–9 per cent of gelatin and intended for Roentgen exposure is mixed with about 400 milligrams of neutralized glyoxylic acid and then cast. The increase of theshold sensitivity amounts to 50–75 per cent. The melting point of the dry layer is 34° C., while the melting point of the unhardened layer is only 32° C. During storage the melting point increases somewhat.

*Example 3*

1 kilo of gelatin silver halide emulsion having a gelatin content of about 8–9 per cent and being sensitized is mixed with 300 milligrams of β-formyl-propionic acid and then cast. The dry layer melts at 36° C. The increase of threshold sensitivity is about 50 per cent.

*Example 4*

1 kilo of gelatin silver halide emulsion having a gelatin content of about 8–9 per cent is mixed with 350 milligrams of γ-formyl-butyric acid and then cast. The melting point of the dry layer

is about 36° C. The increase of threshold sensitivity is about 50 per cent.

We claim:

1. A process which comprises melting gelatin, mixing said gelatin with a compound selected from the class consisting of an aliphatic non-substituted aldehyde carboxylic acid and an aliphatic aldehyde carboxylic acid containing in its molecule a member selected from the class consisting of a hydroxy group, a keto group, and an amino group, and casting said mixture to form a layer.

2. A process which comprises bathing a photographic material consisting of a support and a gelatin layer in a solution of a compound selected from the class consisting of an aliphatic non-substituted aldehyde carboxylic acid and an aliphatic aldehyde carboxylic acid containing in its molecule a member selected from the class consisting of a hydroxy group, a keto group, and an amino group.

3. A process which comprises adding to a photographic silver halide gelatin emulsion containing about 10 per cent of gelatin 0.005 to 0.5 per cent of a compound selected from the class consisting of an aliphatic non-substituted aldehyde carboxylic acid and an aliphatic aldehyde carboxylic acid containing in its molecule a member selected from the class consisting of a hydroxy group, a keto group, and an amino group.

4. A process which comprises adding to a photographic silver halide gelatin emulsion containing 8 to 9 per cent of gelatin 0.02 per cent of formyl-acrylic acid.

5. A process of hardening a protein substance which comprises treating it with a compound selected from the class consisting of an aliphatic non-substituted aldehyde carboxylic acid and an aliphatic aldehyde carboxylic acid containing in its molecule a member selected from the class consisting of a hydroxy group, a keto group, and an amino group.

6. A process of hardening gelatin which comprises treating it with formyl-acrylic acid.

7. A process of hardening gelatin which comprises treating it with glyoxylic acid.

8. Gelatin hardened by the addition of and containing a compound selected from the class consisting of an aliphatic, non-substituted aldehyde carboxylic acid and of an aliphatic aldehyde carboxylic acid containing in its molecule a member selected from the class consisting of a hydroxy group, a keto group and an amino group.

9. A photographic silver halide emulsion layer containing gelatin and a compound selected from the class consisting of an aliphatic non-substituted aldehyde carboxylic acid and of an aliphatic aldehyde carboxylic acid containing in its molecule a member selected from the class consisting of a hydroxy group, a keto group and an amino group.

10. A photographic silver halide emulsion layer containing gelatin and formyl-acrylic acid.

11. A photographic silver halide emulsion layer containing gelatin and glyoxylic acid.

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