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HARDENING PHOTOGRAPHIC LAYERS CONTAINING PROTEINS

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The invention relates to hardened photographic layers, which contain proteins, in particular gelatin as layer forming material, as well as to a process for producing said layers.

During the processing of photographic layers, they pass through various aqueous baths with varying pH values some of which baths have a pH greater than 10. It is extremely important for photographic products to have layers which are more resistant to water, swell to a lesser extent and have a higher layer melting point than pure gelatin layers. This is achieved by treating the gelatin with various substances which are able to react with the gelatin by cross-linking of the protein chains. This process is designated as hardening. Such hardening should not, however, result in the gelatin losing its water permeability. With the known hardening agents hardening is generally started after drying of the layer and reaches its maximum after a few weeks. A large number of compounds are known which are certainly effective, but they harden in a manner which is unpredictable and cannot therefore be accurately controlled, so that when the photographic materials are stored, the sensitometric properties thereof are changed.

The following classes of compounds have been proposed as hardening agents:

Metal salts, such as chromium, aluminum and zirconium salts; aldehydes and halogenous aldehyde compounds, such as formaldehyde, dialdehydes and mucochloric acid; 1,2- and 1,4-diketones, such as cyclohexane-1,2-dione; quinones; chlorides of dibasic organic acids; dianhydrides of tetracarboxylic acids; compounds with several reactive vinyl groups, such as vinyl sulphones, acrylamides; compounds with at least 2 heterocyclic rings which can easily be split off, such as ethylene oxide and ethylene imine; polyfunctional methane-sulphonic acid esters. These hardening agents are compounds of low molecular weight.

Some of them are photographically active and consequently cannot be considered for certain photographic emulsions. Other known compounds having a hardening action are disadvantageous in other respects. For example, metal salts increase the brittleness of the layers, dialdehydes color the layers and anhydrides and acid chlorides have the disadvantage of changing the pH value of the emulsion during the initial hardening. All compounds of low molecular weight have the disadvantage of not hardening specific layers of photographic multilayer materials, since they can penetrate through all layers. In addition hardening with the said hardening agents is not controllable since the hardening starts after drying and increases during storage. This effect is designated as post-hardening. With some photographic paper emulsions, this effect is extremely disturbing, since the tone of the silver image of such papers is changed with increasing period of storage. For photographic papers, more especially brown toning papers, it is consequently important to find a hardener which has little effect when incorporated in the layer, with relatively long storage before processing, and only produces a substantial increase in the layer melting point during development. The papers can then be stored for relatively long periods with only slight effect on the image tone.

As well as the hardeners of low molecular weight referred to above, others which are of high molecular weight are also known. Thus, polyaldehydes, such as the periodic acid oxidation products of starch, have been described as hardeners. However, they have the disadvantage of possessing only a low hardening equivalent, since even in the most favourable case only two aldehyde groups are present to each hexose unit. The maleic acid semiesters of alcohols of high molecular weight, such as polyvinyl alcohol, have similar disadvantages.

German patent specification 1,083,051 discloses a process for the production of compound polymers of polyacrolein, according to which macromolecular polymerisation products of acrolein are reacted with natural or synthetic polymers, which contain groups reactive with carbonyl groups. German patent specification 1,083,051 describes inter alia that the water solubility of gelatin layers can be superfically reduced by water-soluble bisulphite compounds of polyacrolein. The procedure adopted is to treat a gelatin layer, cast on to a glass plate, after drying, with an aqueous polyacrolein-sulphurous acid solution. Since the high polymer hardening agent cannot penetrate into the layer, the hardening of the gelatin only takes place on the surface of the layer. With this hardening method, the hardener is used in relatively very high concentration. In addition, the hardening is not homogeneous. It is an object of the present invention to avoid the disadvantages described above. A further object is to provide a new method for hardening photographic layers which contain proteins as binding agents, thus providing photographic material having excellent physical and photographic properties.

It has now surprisingly been found that protein-containing photographic layers, preferably of gelatin, can be homogeneously hardened at any desired time if water-soluble sulphurous acid adducts of polyacrolein are added to the casting solution at pH values of 4 to 6 and the hardening is started at any desired subsequent time by adjusting the pH value to above 7.

The process utilises the surprisingly strong dependence on pH value of the speed of the cross-linking reaction. When using small quantities of hardener, for example 0.5–4%, the effect is particularly apparent. Completely homogeneous, unhardened mixtures are obtained at pH values of 4–6 with gelatin. The cross-linking reaction proceeds fairly slowly in this pH range, so that there is practically none or only very little hardening. If the pH value is raised to above 7 immediately before casting the layer, then layers are obtained which reach their maximum degree of hardening just after drying. If the pH value is not raised before the casting a hardening action does not, for practical purposes, result even with relatively long storage. It is only by an alkali treatment of the layer that the layer melting point spontaneously rises and layers which are resistant to boiling and handling are obtained. The hardening of the layers can also be achieved by brief treatment of the layers with gaseous ammonia or amines. In each case, swelling and solubility of the layers are reduced to the desired degree and strongly hardened, non-brittle layers, are obtained.

The new hardeners are incorporated into the layers before casting, advantageously as 1–5% aqueous solutions. The viscosity of the casting solution does not rise in practice, even at pH 7. The quantities of substance necessary for the hardening are extremely small. 0.5–4% of the hardener, based on the gelatin dry weight, are sufficient. Layer melting points higher than 100° C. are obtained even by adding 0.5% of hardener.

Water-soluble sulphurous acid adducts of copolymers of acrolein, for example, with styrene or acrylonitrile, are also suitable for the hardening process according to the invention, provided that they have a predominant proportion of acrolein. The sulphurous acid adducts of polyacrolein can be used alone or in admixture with known hardeners such as formaldehyde, mucochloric acid or triacrylformal (German Patent 872,153). In addition, the effect can be increased by adding known hardening accelerators, such as those described by way of example in German patent specification 837,955.

The polyacrolein-sulphurous acid compounds are inactive photographically.

Because of these properties, the hardeners according to the invention provide hitherto unknown possibilities, more especially in the range of photographic applications. The substantial dependence of the speed of the hardening reaction on the pH value and the concentration of the hardener makes it possible for a completely new principle as regards the hardening process to be introduced in the photographic art, which could be designated as "latent hardening." This expression characterises the discovery that, despite the presence of the hardener, the layer is not hardened in practice at pH values of for example 6 and lower. As regards the production of a photographic material, the procedure is that which has already been described above, in which the water-soluble polyacrolein-sulphurous acid compounds are added to the casting solution for the photographic layers at a pH value of about 6, whereupon the layer is cast and dried. In this condition, no hardening reaction occurs. The photographic material is processed in the usual manner, namely, it is exposed, developed and fixed. The hardening reaction is then initiated in an alkali developer bath. This method of procedure excludes the disadvantages of all known hardening agents namely that the image tone or the sensitometric properties of the photographic emulsion layers are changed due to post-hardening during storage. This is explained by the fact that the hardening only occurs when the photographic image has already formed.

Furthermore, the process according to the invention is particularly advantageous with highly sensitive gelatin-silver halide emulsions, the sensitivity of which is undesirably modified by changing the speed of diffusion of the developer. Thus, the use of high-polymer polyacrolein-bisulphite compounds with a molecular weight higher than 3000 also provides the advantage of resistance to diffusion.

When using a dialised polyacrolein-bisulphite compound, the hardener is limited to individual layers. It thus becomes possible for the individual layers of a multilayer coating to be hardened to different degrees. By the use of "latent hardening," the layers are only slightly hardened prior to processing (melting points 50–70° C.). The hardening maximum (higher than 100° C.) is reached in a very short time in alkali baths. The layer bonding of multilayer castings is improved by using these hardening agents.

The sulphurous acid adducts of polyacrolein can be added to a gelatin solution which serves for the production of photographic auxiliary layers, such as intermediate, backing, filter or protective layers or even gelatin-silver halide emulsions which can contain the usual photographic additives and/or dyestuff components and/or spectral sensitisers.

The production of the sulphurous acid adducts of polyacrolein is described in German Patent 1,016,020. The polymers used are prepared in aqueous medium with redox catalysts and the suspension, by transfer into the acid bisulphite compounds, is transformed with sulphur dioxide into aqueous solutions.

After distilling off the excess of sulphur dioxide with water in vacuo, the practically colourless water-soluble acid bisulphite compounds of polyacrolein are obtained, the aqueous solutions of which, after adjustment to the pH value 4, are readily miscible with gelatin.

The polymerisation of acrolein is known from the literature and can be carried out by various processes (e.g. Makromolekulare Chemie, 24, 1957, page 144, and Makromolekulare Chemie, 17, 1955, page 68).

The bisulphite compounds of polyacrolein produced with sulphurous acid are hydro oxysulphonic acids of high molecular weight and as such precipitate gelatin. Consequently, their solutions must be adjusted to pH values between approximately 4 and 5.5 before being added to the gelatin-silver halide emulsions. It is only in this way that completely homogeneous mixtures of gelatin and hardener are obtained. The precipitation of gelatin with the acid polyacrolein-bisulphite compound can be cancelled out by adding sodium bicarbonate solutions. The process is reversible as long as too highly alkaline pH values are not used.

EXAMPLE 1

Different quantities of the bisulphite compound of polyacrolein prepared by the process of German Patent 1,016,020 are added to a silver chlorobromide emulsion containing 60 g. of gelatin per litre, namely, 15 cc., 30 cc., and 60 cc. of a 2% solution of polyacrolein-sulphurous acid compound to 1 litre of emulsion in each case, this substance being added at 40–45° C. at a pH value of 5.5 and while stirring well. The emulsions are provided with the conventional casting additives and cast onto an acetyl cellulose layer support containing a subbing layer. The layer melting points are determined, immediately after a storage time of 24 hours at 50° C. and after processing, i.e. after using the developer and fixing baths and then rinsing.

Quantity of hardener added in percent	0	0.5	1	2
Layer melting point after storage for 24 hours at room temperature, ° C	35	35	38	38
Melting point (° C.) after storage for 24 hours at 50° C	35	40	43	45
Layer melting point after processing, ° C	35	>100	>100	>100

2′ in a developer of the type Agfa 100; 8′ usual fixing, ½ hour rinsing.

The melting point of the layer is raised by the processing in alkali baths. The photographic properties are not changed.

EXAMPLE 2

(a) 3 silver chlorobromide emulsions, each of 1 litre, are brought to the pH values 5.5, 7, and 8.5 and 60 cc. of a 2% polyacrolein bisulphite solution of pH value 4 are than added to each emulsion with stirring. After casting onto a subbed support of a polycarbonate on the basis of bis-4,4′-dihydroxyphenylalkanes and drying the layers, the melting points were determined. The quantity of hardener added was 2%.

pH value of the emulsion	5.5	7	8.5
Melting point after storage for 24 hours at room temperature, ° C	38	>100	>100
Melting point (° C.) after storage for 24 hours at 50° C	54	>100	>100

At the pH value 8.5, the emulsions already solidify on casting.

(b) Quantity of hardening agent added (1%):

pH value of the emulsion	5.5	7	8.5
Melting point after storage at room temperature, ° C	38	69	89
Melting point (° C.) after storage for 24 hours at 50° C	43	76	91

(c) Quantity of hardener added (0.5%):

pH value of the emulsion	5.5	7	8.5
Melting point after storage at room temperature, ° C	35	44	60
Melting point (° C.) after storage for 24 hours at 50° C	40	51	69

The melting points of all layers, after processing as in Example 1, are higher than 100° C. The layers are resistant to handling and show only slight swellability.

EXAMPLE 3

Formation of a multi-layer casting and limited layer hardening

0.9 g. of polyacrolein-sulphurous acid compound (pH 4), prepared by the process of German patent specification 1,016,020, is added to 1 litre of a 6% gelatin solution at pH 6. The mixture is cast onto a subbed acetyl cellulose film (layer 1). After drying, a silver chloride emulsion, which was not hardened, is cast onto the said layer. After drying and storing at room temperature or up to 50° C., the following melting points of the individual layers are obtained.

	Melting point of layer 1, ° C.	Melting point of the emulsion, ° C.
Storage at room temperature	56	38
Storage 24 hours at 50° C	73	38
After processing	100	38

After processing, the melting point of the emulsion has not changed, since the dialysed bisulphite compound of high molecular weight is resistant to diffusion and does not migrate. Layer 1 as, however, become hardened so as to be resistant to handling and boiling. The emulsion layer can be removed by simple washing off with hot water.

The sulphurous acid adducts of polyacrolein according to the invention can be understood as usual bisulfite-addition compounds, which are generally obtained by the characteristic reaction of aldehydes with, e.g., sodium bisulfite solutions. The aldehyd-groupings of the polyacrolein are substantially transformed in a hydroxysulphonic acid group of the bisulfite-addition product.

Copolymers of acrolein which can be used as hardening agents according to the invention in the form of the bisulfite addition compounds are described, for example, in Houben-Weyl, "Methoden der organischen Chemie," volume XIV/1, page 1086. Suitable components for acrolein are amongst others acrylonitrile, acrylic acid, acrylic acid esters, acrylamide, styrene, vinylacetate etc. The copolymers should contain at least 50 mol percent of acrolein. The bisulfite-addition compounds of the copolymers are prepared according to methods suitable for polyacrolein-bisulfite addition products.

Having thus described our invention, we now state that we believe our invention to be capable of numerous variations in the bisulfite-addition compound, the photographic layers to be hardened and the kind of alkaline baths which are used to initiate the hardening reaction.

The composition of the said baths are not critical, they only have to cause the adjustment of the pH-value in the protein layers to values of above 7.

According to a preferred embodiment of the invention, the alkaline developer solution can be used for this purpose, whereby the hardening reaction is neither influenced by the kind or the chemical structure of any developers nor by any other ingredients being present in such developer baths.

The kind of the alkaline agent of said treating bath is not especially critical and can be selected according to the requirements of the protein layer, which is to be hardened. Suitable are, for example, hydroxides, carbonates, phosphates or borates of alkali metals, such as sodium or potassium. Furthermore, hydroxides of earth alkali metals, such as calcium or barium hydroxides and ammoniac or organic amines.

We claim:

1. A process for hardening photographic light-sensitive protein layers and photographic auxiliary protein layers comprising forming a mixture containing photographic protein and as a hardening agent a water-soluble bisulfite of a member selected from the group consisting of polyacrolein and copolymers of acrolein containing at least **50** mol. percent acrolein while maintaining the pH of the mixture between 4 and 6, casting said mixture on a support at a pH of between 4 and 6 and subsequently raising the pH of the cast mixture to above 7 whereby hardening is effected.

2. A process for hardening photographic light-sensitive gelatin layers and photographic auxiliary gelatin layers which comprises forming a mixture containing photographic gelatin and from 0.5 to 4 percent by weight based on dry weight of gelatin of a hardening agent selected from the group consisting of polyacrolein and copolymers of acrolein with a monomer selected from the group consisting of acrylonitrile, acrylic acid, acrylic acid ester, acrylamide, styrene and vinylacetate containing at least 50 mol percent acrolein while maintaining the pH of the mixture between 4 and 6, casting the mixture on a support at a pH between 4 and 6 and subsequently raising the pH of the cast mixture to above 7 whereby hardening is effective.

3. A process according to claim **1** wherein the copolymers of acrolein are copolymers with a monomer selected from the group consisting of acrylonitrile, acrylic acid, acrylic acid ester acrylamide, styrene and vinylacetate.

4. A process for hardening photographic gelatin layers which comprises

(a) mixing at a pH value of between 4 and 6 an aqueous casting solution for the photographic gelatin layer with an aqueous solution of a water soluble bisulfite compound of a member selected from the group consisting of polyacrolein and copolymers of acrolein which contain at least 50 mol percent acrolein with a monomer selected from the group consisting of acrylonitrile, acrylic acid, acrylic acid esters, acrylamide, styrene and vinylacetate, the bisulfite compound being present in an amount of 0.5 to 4% by weight, based on the dry weight of gelatin;

(b) casting the mixture of the casting solution for a photographic gelatin layer and the aqueous solution of the water-soluble bisulfite onto a support to form an unhardened layer having a pH of between 4 and 6;

(c) drying the photographic gelatin layer thus formed; and

(d) raising the pH of that unhardened photographic gelatin layer to above 7, thereby hardening that photographic gelatin layer.

5. A process as defined in claim **4** wherein an aqueous solution of an additional hardener selected from the group consisting of formaldehyde, mucochloric acid and triacrylformal is added to the mixture of the casting solution for the photographic gelatin layer and the aqueous solution of the water-soluble bisulfite compound.

6. A process as defined in claim **4** wherein the pH of the unhardened photographic gelatin layer is raised to above 7 by treating that photographic gelatin layer with an alkaline developing bath.

7. A process as defined in claim **4** wherein the casting solution for the photographic gelatin layer is mixed with an aqueous solution of the water-soluble bisulfite of polyacrolein.

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