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[54] **PHOTOGRAPHIC MATERIAL WITH NC-LAYER**
3 Claims, No Drawings

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A, 84

[56] **References Cited**

UNITED STATES PATENTS

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ABSTRACT: A photographic material which has an NC-layer comprising an acrylamide copolymer.

PHOTOGRAPHIC MATERIAL WITH NC-LAYER

This invention relates to a photographic material which has an NC-layer which provides improved anticurling properties.

Coating of a support of cellulose acetate, polyester, or polycarbonate or a similar macromolecular film-forming substance is covered with a photographic layer on one side courses the support to curl after drying towards the coated side. In photographic technology, this tendency to curl up is counteracted by coating the rear surface of the support with a so-called NC-layer (noncurling layer) or, where this is not possible, the support is treated with a solvent in order to produce a certain preliminary curling towards the opposite direction.

In addition, the tensile forces within the photographic layers can be reduced by incorporating synthetic resin dispersions in the layer.

In order to ensure the flatness of photographic films under different climatic conditions, gelatin-backing layers are preferably used in practice. To compensate for the tensile forces which occur in multilayered photographic materials in which the total thickness of the layers may amount to 28μm., it is necessary to apply thick NC-layers of gelatin to the rear surface. The casting of gelatin layers of about 20μin thickness in a single process step requires a special-casting technique and removal of the large quantities of water from the layers, requires casting machines with long-drying devices and high-drying capacities. Moreover, it is necessary to dry relatively slowly in order to prevent wrinkling of the layer and brittleness. For some types of photographic film, thick NC-layers are undesirable for taking the photographs and for processing the films. Thus, for example, the length of film per spool or cassette unit would have to be reduced in cine films or amateur gelatin NC-layers are applied. Furthermore, gelatin NC-layers are difficult to process in continuous processing machines owing to their high tendencies to swell and their low wet strength (risk of scratching on the rolls).

It is among the objects of the invention to provide NC-layers which even if the layers are thin show a high anticurling effect and improved scratch resistance.

We now have found a photographic material comprising at least one supported light-sensitive silver halide emulsion layer and an NC-layer on the rear surface of the support, wherein the binding agent for the NC-layer consists of at least 80 percent by weight based on the total amount of the binding agent of

65–80 percent by weight of acrylamide,
2–25 percent by weight of acrylonitrile
2–percent by weight of acrylic acid acrylonitrile, methacrylic acid, and
0–20 percent by weight of an alkyl ester of acrylic or methacrylic acid,
and up to 20 percent by weight of gelatin.

The copolymers for use according to the invention preferably have intrinsic viscosities of 1.5 to 3.5 100 ml./g. and average molecular weights of 5,000 and 100,000.

Suitable esters which are copolymerisable with the above monomers and which are particularly suitable are the lower alkyl esters of acrylic acid such as methyl acrylate, ethyl acrylate, propyl acrylate, isopropyl acrylate, β-hydroxyethyl acrylate, β-hydroxypropyl acrylate and the corresponding methacrylic acid esters.

The copolymers are substantially free from low molecular weight constituents and may be applied directly on to the support as highly viscous aqueous solutions.

The noncurling characteristics of the layer as well as the abrasion resistance are highly improved by cross-linking or hardening the copolymer gelatin mixture with hardening agents. The following hardeners are suitable for the process of the present invention:

I. Aliphatic aldehydes such as formaldehyde; hydroxy aldehydes e.g. glycolaldehyde, aldol or glyceroladehyde; dialdehydes, for example glyoxal, glutaraldehyde, succinic or methoxysuccinic dialdehyde; unsaturated aldehydes, e.g. acrolein, crotonaldehyde or polymers thereof and their bisulfite adducts; aldehyde acids and their halogen derivatives such as muc-obromicor -chloric acid;

II. Aliphatic α- or γ-diketones;

III. Ethylene oxide derivatives containing at least two epoxide groups separated from each other by an aliphatic radical, the cyanuric acid group or a group derived from an aliphatic carboxylic or sulfonic acid or from an inorganic acid. Suitable compounds are described in U.S. Pat. No. 3,047,394 or German Pat. No. 1,095,113. Particular utility is exhibited by 1,2-bis-(1',2'-epoxypropoxy)ethane or 1,4-bis-(1',2'-epoxypropoxy)butane.

IV. Triazine derivatives containing at least two hardening groups in particular halogenated triazines such as described in U.S. Pat. No. 3,288,775, British Pat. No. 1,022,656 or German Offenlegungsschriften 1,522,378 or 1,900,791. Particular reference is made to 2-(2'-methoxyethoxy)-4,5-dichloro-*s*-triazine or 2-isopropyloxy-4,6-dichloro-*s*-triazine.

One may also use mixtures of several of these hardeners. The hardening process can be accelerated by means of hardening accelerators such as 1,4-diaza-bicyclo-[2,2,2]-octane, N,N'-dimethylpiperazine, 2-methylpyridine, trimethylamine, triethylamine and similar tertiary amines.

The copolymers, like gelatin, have the properties of a hydrosol and are very suitable for improving the anticurling properties of the photographic material even under extreme climatic conditions. The noncurling layer of the present invention can be applied to the rear surface of any photographic materials which tend to curl towards the side which has been coated with emulsion layers owing to very high tensile forces, particularly multilayered color photographic materials. The photographic supports may consist of the material customarily applied in the art such as cellulose esters, polycarbonates, especially those based on bisphenylolalkanes, polyesters, preferably those based on terephthalic acid and ethylene glycol.

The copolymers for use according to the invention are photographically inactive, miscible with gelatin in any proportion and abrasion resistant when hardened.

The NC-layers of the present invention form a clear layer which is advantageous over pure gelatin layers in that a thinner layer is sufficient to provide the necessary anticurling properties of the film and in that they can be cast more rapidly owing to their better drying properties.

Another advantage over gelatin is that they can be prepared more uniformly.

The layers according to the invention may also be used for stiffening polyester layer supports. This makes it possible to use extremely thin polyester layer supports so that the length of film in the usual cassettes can be increased.

The copolymers are prepared by known polymerization processes. A particularly advantageous method of preparation is the polymerization in water in the presence of water-soluble radical-forming agents at temperatures of between 10 and 95° C. The aqueous polymer solutions obtained can be used directly as layer-forming substances. Aqueous polymer suspensions are preferably converted into solutions by the addition of small quantities of alkali.

Copolymers of the following composition are given as examples:

	Copolymers						
	1	2	3	4	5	6	7
Percent:							
Acrylic acid amide	75	70	72.5	70	75	72.5	67.5
Acrylic acid	5	10	7.5	10	5	7.5	10
Acrylonitrile	20	5	5	7.5	5	5	5
Ethyl acrylate		15	15				
Hydroxypropyl methacrylate				12.5	15	15	
Methylacrylate							17.5

The NC-layers according to the invention are produced by the usual methods. Casting solutions of the following composition may, for example, be used: 1 l. of a 10–15 percent aqueous polymer solution

10–200 ml. of a 10 percent aqueous gelatin solution and
100–300 ml. of a 5 percent aqueous solution of one or more of the above mentioned hardeners.

After the addition of 50 ml. of a 5 percent saponin solution and adjustment of the viscosity to the value which is required for a given casting system by dilution with water, the casting solution is applied onto the support in a thickness of 2 to 10μ. The layer can be applied by the known casting processes.

The usual additives for NC-layers, e.g. matting agents, antistatic agents, antihalation dyes such as colloidal silver, etc. can easily be added.

EXAMPLE 1

120 ml. of a 10 percent aqueous gelatin solution,
50 ml. of a 5 percent aqueous mucochloric acid,
70 ml. of 2-(2'-methoxyethoxy)-4,6-dichloro-s-triazine (5 percent in dioxane),
50 ml. of a 5 percent saponin solution and
1 l. of distilled water are added to 1 l. of a 12 percent aqueous solution of copolymer I.

This casting solution is applied by immersion onto a support of cellulose acetate which is 95μ thick, the casting solution being applied to form a final layer of thickness 5μ. After drying, an abrasion resistant NC-layer which curls to a considerable extent towards the coated side and which has a melting point of over 100° C. is obtained.

The other side of the support is coated with a silver bromide gelatin emulsion layer of thickness about 8μ, and a protective layer of about 1μ. The material produced in this way does not curl at room temperature and 60 percent relative humidity and shows practically no curling after storage in a heating cupboard at 50° C.

EXAMPLE 2

100 ml. of a 10 percent aqueous gelatin solution,
100 ml. of a 5 percent aqueous solution of 1,2-bis(1',2'-epoxypropoxy)ethane,
50 ml. of a 5 percent aqueous saponin solution and
500 ml. of distilled water are added to 1 l. of a 10 percent aqueous solution of copolymer II. This casting solution is applied to a support of cellulose acetate which is 95 μ thick to give a layer about 10μ thick.

After drying, silver halide emulsion layers containing the usual color-forming couplers for a color photographic multilayered material are applied to the other side of the support to give a total thickness of 20μ. This final film does not curl under the conditions given in example 1.

EXAMPLE 3

An NC-layer 5μ in thickness as described in example 2 is applied onto an 85μ thick support of polyethylene glycol terephthalate, and the silver halide emulsion layers required for a color photographic reversal material are applied (total thickness 14μ) to the other side. The film has a good stiffness and an excellent mechanical stability and does not curl.

EXAMPLE 4

70 ml. of a 5 percent solution of 1,4-bis-(1',2'-epoxypropoxy)butane in dioxane,
80 ml. of 2-(2'-methoxyethoxy)-4,6-dichloro-s-triazine in dioxane and
20 ml. of a 10 percent aqueous solution of 1,4-diazabicyclo-[2,2,2]-octane are added to 1 l. of a 15 percent aqueous solution of copolymer III and cast on a 200μ thick support of cellulose acetate to give a layer of thickness 10μ from a casting apparatus which has a horizontal solidification and drying device at 60° C. It is then dried at 100° C. for 5 minutes. The silver halide emulsion layers containing color coupler necessary for a color photographic reversal material are applied onto the other side as in example 3. The photographic film thus produced does not curl.

Similar results are obtained with copolymers 4–7.

We claim:

1. A photographic material having at least one supported light-sensitive silver halide emulsion layer and one NC-layer on the rear surface of the film support, wherein the binding agent for the NC-layer consists of at least 80 percent by weight based on the total amount of the binding agent of a copolymer containing 65 to 80 percent by weight of acrylamide, 2 to 25 percent by weight of acrylonitrile, 2 to 15 percent by weight of acrylic acid or methacrylic acid and 0 to 20 percent by weight of an acrylic acid alkyl ester or a methacrylic acid alkyl ester, the alkyl group of which may be substituted by hydroxyl groups, and up to 20 percent by weight of gelatin.

2. The material of claim 1, wherein the NC-layer is hardened with hardeners.

3. A process for making NC-layers by applying the solution for the NC-layer onto the rear side of a film support containing on the front side at least one light-sensitive silver halide emulsion layer and drying the NC-layer, the improvement consisting of applying to the support a casting solution for the NC-layer the binding agent of which consists of a mixture of at least 80 percent by weight based on the total amount of the binding agent of a copolymer containing 65 to 80 percent by weight of acrylamide, 2 to 25 percent by weight of acrylonitrile, 2 to 15 percent by weight of an acrylic acid alkyl ester or a methacrylic acid alkyl ester, the alkyl group of which may be substituted by hydroxyl groups, and up to 20 percent by weight of gelatin, and hardening agents for the said binding agents comprising an aliphatic aldehyde, an aliphatic epoxide containing at least two epoxide groups or a bis-halogeno-s-hexahydrotriazine.