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3,558,316

PHOTOGRAPHIC MATERIAL CONTAINING AN OPTICAL BRIGHTENING AGENT

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5 Claims

ABSTRACT OF THE DISCLOSURE

A photographic material which contains a water-insoluble optical brightening agent mixed with an anionic polyurethane heterogeneously dispersed in a gelatin layer.

This invention relates to photographic material which contains an optical brightening agent and which comprises at least one gelatin-containing photographic layer the physical properties of which are improved by the use of water-insoluble optical brightening agents contained in anionic polyurethanes which serve as carriers.

The optical brightening agents used in photography to increase the degree of whiteness of photographic materials on a paper support are largely water-soluble compounds. They are present in the light-sensitive silver halide emulsion layers, in gelatin layers which contain color components, in the baryta layers and other auxiliary layers. In practice the water-soluble optical brightening agents which are not diffusion-resistant are washed out to a considerable extent when left to stand in water for prolonged periods, and the optical brightening effect is then correspondingly reduced. In order to overcome this disadvantage, it has already been proposed to incorporate the optical brightening agents in the layers in a diffusion-resistant form. The known methods employed in photography, e.g. incorporation by emulsification may be used for this purpose. In this process, the organic brightening agents which are insoluble in water are dissolved in a high boiling organic solvent or in a solution of a resin, and incorporated in the casting solution for the photographic layer.

Although the disadvantages described above are reduced to a certain extent, the known processes are unsatisfactory since they do not meet the high requirements which are required in the photographic art. The brightening agents employed by the emulsification process have to meet various requirements. They should be insoluble in water and readily soluble in the organic medium. Since the brightening agents are present in the layer together with the solvent medium, both the brightening agents are present in the layer together with the solvent medium, both the brightening effect of the optical brightening agents and their light fastness in combination with the particular medium employed must satisfy the requirements. The known processes and combinations of brightening agents with organic solvents are particularly unsatisfactory with respect to these last properties.

An object of this invention is to provide photographic materials on paper supports which contain optical brightening agents which are incorporated in a diffusion resistant manner and which have sufficient brightening effect and fastness to light.

We now have found that optical brightening agents which are substantially water-insoluble can advantageously be incorporated into photographic layers in admixture

with an anionic polyurethane, which mixture is emulsified into the casting solution for the photographic layer.

The photographic layer contains the mixture of the anionic polyurethane and the optical brightening agent in emulsified form, whereby the optical brightening agent is contained in the finely distributed droplets of the anionic polyurethane.

The anionic polyurethanes described in French Pat. 1,471,609 are excellently suitable for photographic materials of the invention. They are prepared from high molecular weight compounds which have a molecular weight of 300 to 10,000 and contain several reactive hydrogen atoms, polyisocyanates and, if desired, chain lengthening agents with reactive hydrogen atoms. In a preferred embodiment, compounds which contain at least one active hydrogen atom and at least one salt-type anionic group or anionic group capable of salt formation are incorporated in the polymer. If compounds which contain anionic groups that are capable of salt formation are employed, the resulting anionic polyurethanes are subsequently at least partly converted into the salt form. Particularly suitable anionic groups are sulfo or carboxyl groups, and in order that the water-insoluble optical brightening agents should be sufficiently compatible with the polyurethane, the proportion by weight of the anionic groups should be more than 0.1 and less than 8%, preferably 0.5 to 4%.

The starting components used in the preparation of the polyurethane dispersions are described in more detail in French Pat. 1,471,609.

Particularly suitable polyurethane for use according to this invention are those which are prepared from polyhydroxyl compounds, such as the known polyesters, polyethers, polycarbonates and polyacetals which have molecular weights of 300 to 10,000, preferably 600 to 4000, diisocyanates which have aliphatic isocyanate groups, such as 1,6-hexane-diisocyanate, 1,4-butanediisocyanate, hexahydrotoluylene diisocyanate, dodecane hydrodiphenylmethane diisocyanate, 1,3-, respectively 1,4-xylene diisocyanate, 1,4-cyclohexylene diisocyanate and alkali metal salts of aliphatic amino acids such as taurine, methyl taurine, glycine, lysine, ornithine and addition products of propane sultone or butanesultone to aliphatic diamines such as ethylene diamine or hexamethylene diamine.

The optical brightening agents which are used are those which are insoluble in water and highly compatible with anionic polyurethanes. Suitable optical brightening agents include those of the following groups:

(I) Coumarin derivatives such as:

3,7-phenylaminocoumarin and its derivatives,
3-benzoxazole coumarin derivatives

(see e.g. German Auslegeschriften DAS Nos. 1,090,624, 1,020,636, 1,102,694 and 1,098,125).

(II) Stilbene derivatives such as:

stilbyl benzotriazoles
stilbyl oxazoles,
stilbylbenzene-1,3,4-oxadiazoles,
4,4'-dibenzoxazoly-stilbenes,
bis-triazinylaminostilbene derivatives

(see e.g. French Pats. Nos. 1,397,201 and 1,293,281 and Belgian Pat. No. 624,472).

(III) Azole brightening agents such as thienyl azole derivatives, e.g. 2-aroxyozoly-5-arylthiophenes (see also e.g. Belgian Pat. No. 617,370 and French Pat. No. 1,233,914). Triazolyl azole derivatives such as those described in U.S. Pat. No. 2,715,632 and French Pats. Nos. 1,172,134 and 1,368,515 and Belgian Pat. No. 631,859. Dibenzoxazoly-2-ethylene compounds, e.g. according to those described in Belgian Pats. Nos. 601,165/66 and U.S. Pat. No. 3,147,253.

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(IV) Pyrazolo-quinoline compounds (see German Auslegeschrift No. 1,222,889).

Other suitable brightening agents are described in the book by E. Uhlein "Optical brightening agents" 1957, Moser Verlag, Garmisch-Partenkirchen.

When preparing the photographic materials according to the invention, the aqueous dispersions of anionic polyurethane containing the water-insoluble optical brightening agent are added to the casting solutions for the given layer. The polyurethane particles are then present in the finished layer in heterogeneous distribution although they are not optically detectable, and these polyurethane particles in turn contain, dissolved therein, the optical brightening agents which are soluble in these particles but not in the layer itself.

The aqueous anionic polyurethane dispersions which contain the water-insoluble optical brightening agents may be prepared by the following general method:

The polyhydroxyl compound is dehydrated under a water jet vacuum at 120° C. for 30 minutes and is then reacted with the diisocyanate. After the prepolymer has been cooled to 50 to 55° C., the melt is dissolved in a low boiling organic solvent such as acetone or tetrahydrofuran and reacted with the compound which contains reactive hydrogen atoms and anionic salt groups. Water or methanol is used as solvent for this compound. After the polyaddition reaction is complete, the water-insoluble optical brightening agent is added to the reaction mixture as a solution in a low boiling organic solvent such as acetone, tetrahydrofuran or methanol. Alternatively, the optical brightening agent may be added to the organic prepolymer solution, or at an earlier stage to the prepolymer or any one of its components before the addition of the compound which contains anionic salt groups and reactive hydrogen atoms. In that case, however, only those optical brightening agents which do not contain any groups which are reactive with isocyanate groups may be used.

In order to disperse the polyurethane solution which contains the optical brightening agent, the quantity of water calculated for a given solids content of the dispersion is stirred in and the organic solvent present in the reaction mixture from which the dispersion is obtained is distilled off in vacuo. The resulting aqueous polyurethane dispersion which contains the optical brightening agent which is insoluble in water is added directly to the casting solutions for the layers.

The concentration of brightening agent in the polyurethane or the quantity of polyurethane added to the photographic layer may vary within wide limits. It depends on the purpose for which the layer is to be used, the nature of the layer and the particular photographic process for which the photographic material is intended. Concentrations of 0.05 to 5%, preferably 0.2 to 2%, of optical brightening agent based on the dry weight of the mixture of polyurethane and brightening agent are generally adequate for obtaining a brightening effect. The concentration in the layer of the polyurethane which contains brightening agent amounts to 0.05 to 50 and preferably 0.1 to 40 parts by weight part by weight of gelatin. The aqueous polyurethane dispersions added to the casting solutions contain about 20 to 60, preferably 30 to 50%, of the mixture of polyurethane and brightening agent.

The dispersions of polyurethane and brightening agent may be added to all types of photographic layers, for example, silver halide emulsion layers which may contain color couplers, or other photographic auxiliary layers such as protective filter layers or baryta-coatings.

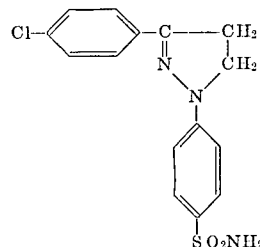
EXAMPLE 1

Preparation of the dispersion of polyurethane and brightening agent

251 g. of a polyester of adipic acid, 1,6-hexanediol and neopentyl glycol (molar ratio 30:22:12; OH number 66.6)

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are dehydrated in a water jet vacuum for 30 minutes at 120° C., and 39.1 g. of 1,6-hexanediisocyanate are added at 90° C. After these components have reacted together for 2 hours at 120° C. the prepolymer is cooled and dissolved in 620 ml. of acetone. 41.1 g. of a 20% aqueous sodium taurinate solution are stirred into the acetonic prepolymer solution which is at a temperature of 50° C. After completion of the reaction, 6 g. of a water-insoluble optical brightening agent of the following formula:



dissolved hot in 250 ml. of acetone are added. 620 ml. of water are then stirred in. After the reaction mixture has been stirred for a short while longer, the acetone is distilled off under a water jet vacuum at 50° C. The anionic polyurethane dispersion obtained has a polyurethane content of 42% and the polyurethane contains 2% of optical brightening agent.

Preparation of the photographic material

An aqueous solution for application by spreading is prepared from 20 kg. of barium sulfate, 7.5 l. of a 25% aqueous gelatin solution, 1 l. of a 10% chrome alum solution and 4 l. of the above aqueous polyurethane dispersion, with stirring. This is then applied to a paper support and the resulting layer is dried. A photographic silver chlorobromide gelatin emulsion layer is then applied on this baryta layer in the usual manner.

The dry layer is processed in the usual manner to form a photographic silver image. The final image is of exceptionally high quality owing to the high degree of whiteness of the baryta layer. No diffusion of the optical brightening agent into the development or fixing bath can be observed.

EXAMPLE 2

A photographic black-white emulsion which contains 10 g. of silver in the form of a mixture of silver chloride and silver bromide, 140 g. of gelatin and 100 g. of the polyurethane dispersion used in Example 1 is applied to a baryta paper support and dried. In addition to possessing substantially reduced friability, the paper is distinguished by a high degree of whiteness. The sensitivity, tendency to fogging, gradation and brilliance are not altered by the addition of the dispersion which contains the water-insoluble optical brightening agent.

After processing, a photographic silver image of excellent quality is obtained. The brightening agent was not lost by diffusion during processing.

EXAMPLE 3

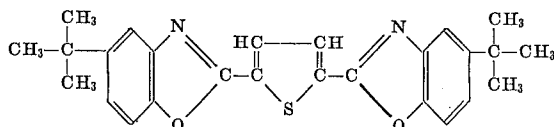
80 g. of the polyurethane dispersion used in Example 1 are introduced with stirring into 1 kg. of a silver bromide gelatin emulsion which has a gelatin concentration of 8% and which contains 3-(p-stearyl-amino-benzoylacetamide)-isophthalic acid as yellow coupler. After usual processing, a particularly brilliant photographic color image is obtained on an excellent white support. The brightening agent was not lost by diffusion during processing.

EXAMPLE 4

The same procedure is used in the preparation of the polyurethane dispersion as in Example 1. However, instead of using the optical brightening agent mentioned in

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Example 1, 6 g. of the brightening agent of the following formula are used in analogous manner:



The polyurethane dispersion obtained has a polyurethane content of 40% and the polyurethane itself contains 2% of optical brightening agent. This dispersion is then used in the production of the photographic material in the same manner as in Examples 1, 2 and 3. The resulting layers and paper films have exceptionally good fastness to light together with high diffusion resistance.

EXAMPLE 5

The same procedure is employed as in the preparation of the polyurethane dispersion of Example 1, except that, instead of the brightening agents mentioned in Examples 1 and 4, 4.5 g. of an optical brightening agent of the type described in French Pat. No. 1,480,699 is used in an analogous manner.

The polyurethane dispersion obtained has a polyurethane content of 38.5% and the polyurethane contains 1.5% of optical brightening agent. This dispersion is used in the preparation of a baryta color for coating in a manner analogous to that used in Example 1.

These layers are distinguished by their exceptionally high fastness to light, together with their high diffusion fastness.

We claim:

1. Photographic material comprising at least one silver halide emulsion layer on a paper support which is provided with a baryta layer, characterized in that 0.05 to 50

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parts by weight per 1 part by weight of gelatin, of particles of an anionic polyurethane are heterogeneously distributed in gelatin in at least one of the layers, these particles containing dissolved therein an optical brightening agent which is insoluble in water.

2. Photographic material as defined in claim 1, characterized in that the optical brightening agent is present in the anionic polyurethane in a quantity of 0.05 to 5%.

3. Photographic material as defined in claim 1, wherein the anionic polyurethane is a sulfonated or carboxylated polyurethane of essentially a linear compound that has two terminal hydroxyl, carboxyl or amino grouping and also has a molecular weight of 300 to 20,000.

4. Photographic material according to claim 3, characterized in that the proportion by weight of sulfonic or carboxyl groups present in the polyurethane is 0.1 to 8%.

5. Photographic material according to claim 1, characterized in that the anionic polyurethane and the optical brightening agent are present in the baryta layer.

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U.S. Cl. X.R.

96—85; 117—33.5; 252—301.2