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METHOD FOR OPTICAL BLEACHING OF COATED PHOTOSENSITIVE PAPERS AND RESULTANT PRODUCT

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No Drawing. Original application June 2, 1958, Ser. No. 739,211, now Patent No. 3,047,390, dated July 31, 1962. Divided and this application June 11, 1962, Ser. No. 201,300

Claims priority, application Netherlands, June 6, 1957, 217,900

8 Claims. (Cl. 96—82)

The present invention relates to a process for whitening, i.e. optical brightening, the surface color of paper, especially photographic paper, provided with one or more surface coatings composed of constituents which are not capable of strongly binding the usual optical bleaching agents, and more particularly relates to a process for brightening the white areas in the photographic image of a photographic layer in such a way that the diffusion of optical bleaching agents out of the photographic layer is inhibited.

It is generally known that the reflecting power of a paper surface can be considerably increased by applying thereto a surface coating containing finely divided fillers, which are usually pigments, having a high degree of whiteness. Examples of fillers used for this purpose are titanous dioxide, barium sulfate, zinc sulfide, calcium carbonate and silicium dioxide, among others. In this way, the surface color of the paper can be whitened to a certain extent, but not completely. If, however, these pigments are used in conjunction with substances which are slightly colored or acquire coloration in the course of further treatment or after storage, as for example where such substances either are included in the same surface coating with the pigments or are present in one or more additional surface layers, the brightening effect attributable to the pigment is nullified wholly or partially. Thus, it is seen, for instance, that when a baryta-coated paper support is coated with a photographic emulsion, the surface color of the photographic paper is not completely white and even the whitest areas in a photographic image obtained upon such a support will still absorb a considerable amount of light. This coloration depends on various factors, such as the reflecting power of the paper used, the quality of the gelatin applied as binding agent for the photographic layers, and the kind and the amount of other compounds present, such as, e.g. sensitizing dyestuffs added to the photographic layers during the manufacture of the light-sensitive element. This coloration can also be caused by colored decomposition products formed in the photographic layers as they are subjected to development and/or other treatment or formed in the treatment baths and absorbed by these layers as they are immersed therein. Since the cellulose fibers from which the paper is composed, as well as the gelatin used as binding agent for the photographic layers and the decomposition products which are formed during processing, absorb light particularly in the range of the short wave-lengths, the photographic paper shows in most cases a slight yellow tinge.

It has been proposed to eliminate this defect by adding to the paper support, to a surface coating and/or to another superposed layer, dyestuffs or pigments which absorb in the range of the long wave-lengths, so that the spectral character of the reflected visible light is equal to that of the incident visible light and the paper, consequently, shows a neutral tone. Thus, it is known to add organic,

light fast, blue dyestuffs to a baryta-coating which is applied to a paper support destined to receive a photographic emulsion layer.

As an inherent result of the latter expedient, the incident visible light is not completely reflected but partly absorbed by the yellow paper and partly by the blue dyestuff or the blue pigment. Even under the most favorable circumstances where only an extremely small amount of dyestuff or pigment is required, such as for instance, in the case of a photographic paper manufactured from a baryta-coated base stock of good quality and containing a little colored gelatin and one or more sensitizing dyestuffs of the type which during the processing can easily be removed from photographic layers, the whitest areas in the photographic image will not completely reflect the visible light.

According to a more recent proposal, substantially colorless, blue-fluorescing, ultraviolet-absorbing compounds are added during the manufacture to the paper or to one or more surface coatings. These compounds absorb ultra-violet radiation of between about 3000 Angstrom units and 4000 Angstrom units and emit fluorescent light of between 4000 Angstrom units and 5500 Angstrom units and are commonly referred to in the art as optical bleaching agents. They can be added during the manufacture of a photographic paper, either to the paper support, to the layer wherein the photographic image is formed (for instance, the silver halide emulsion layer) or to a layer therebetween (for instance, a baryta-coating). The photographic element can also be treated with a solution of such compounds during processing.

The spectral partition of the reflected visible light is equalized by the use of these optical bleaching agents to that of the incident visible light by conversion of a part of the incident ultra-violet rays to which the human eye is not sensitive into the blue light absorbed by the paper. The reflected light is now completely neutral, without loss of any part of the visible incident light. By applying this concept to the manufacture of photographic paper, not only is it possible to obtain a neutral image tone together with a strong reflecting power of the white areas in the photographic image, but photographic images to be viewed by reflection can even be manufactured which reflect more visible light than they actually receive. The latter result can be achieved by the use of an excess of optical bleaching agent, so that more ultra-violet light is converted into blue light than is necessary to correct the yellowness of the photographic paper. In this way, one can change the image-tone to a colder, i.e., more bluish, tone.

In connection with the process just described, it is to be noted that if the optical bleaching agent is added to the paper alone, insufficient brightening of the images is obtained, since the whitening effect is annulled in large measure by the superposed baryta-coating which is present in most of the photographic papers.

It is evident that the degree of success obtained in the practice of the above-mentioned process depends heavily on the amount of optical bleaching agent which still remains in the completely finished paper. Consequently, efforts have been made in the past to prevent the removal of optical bleaching agents, either in whole or in part, from the layers of the photographic element wherein they appear, as can happen when the element is treated in the usual treating baths.

None of the various suggestions for combating the tendency of the optical bleaching agents to wander, i.e. diffuse, out of the emulsion layer and/or the baryta-coating has hitherto been found wholly effective.

Summarizing, the great difficulty in finding an effective solution to the problem of loss of optical bleaching

agents from photographic elements during processing is attributable mainly to the fact that optical bleaching agents are not sufficiently adsorbed on the materials, such as gelatin and baryta, of which the usual surface-coatings applied to photographic paper are composed.

It is therefore an object of the present invention to provide a method for increasing the whiteness of the surface of a paper provided with an optical bleaching agent and at least one surface coating whereby the wandering of the optical bleaching agent out of its original locus is inhibited. It is a further object of the present invention to provide a method for increasing the whiteness of photographic papers. Still further objects and advantages will appear in the following description and examples.

In accordance with the present invention, it has now been found that the wandering or diffusion of optical bleaching agents out of the layers in which they were initially incorporated can be inhibited at least substantially completely by treating certain finely divided water-insoluble macromolecular products with a solution or a dispersion of an optical bleaching agent having a pronounced substantivity to the macromolecular product used and then adding the fluorescing mass thus obtained to one or more surface coatings for the paper. In the manufacture of photographic paper, for example, the fluorescing mass can be incorporated into a layer between the paper support and the layer wherein the photographic image is formed or into the latter layer itself.

Our parent application, Serial No. 739,211, filed June 2, 1958, now Patent No. 3,047,390, originally disclosed as suitable macromolecular products for the practice of the invention, certain cellulosic, polyester, polyamide and urea-formaldehyde resins but was eventually restricted to the polyester subject matter. This application is directed to the urea-formaldehyde subject-matter divided out of said patent application while applications Serial No. 201,298 and No. 201,299, filed concurrently herewith, are directed, respectively, to the cellulosic and polyamide resin subject-matter thereof.

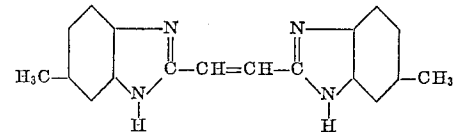
For best results, the urea-formaldehyde resin utilized herein is prepared according to the method disclosed in British specification 614,919.

The reaction products of the method of the British patent are infusible and insoluble. These products are particularly well adapted for incorporation in the silver halide photographic emulsion layer of a photographic paper. Finely divided particles of the resin can be obtained directly from the initial condensation reaction, i.e. primary resin stage, by spray-drying. Catalysts may, of course, be included to promote further polymerization at a later stage. Whether obtained by spray-drying or not, the polymer must be aged or cured by drying under controlled conditions to allow the polymerization to advance to the requisite end-point. When dried, the resin may be reduced by grinding or further pulverized in the case of spray-dried particles until the desired degree of fineness has been obtained.

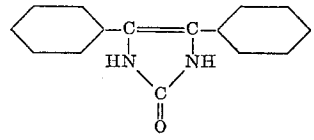
If not already in this condition, the urea-formaldehyde resin, before use, is reduced to finely divided form. The subdividing operation may be carried out in a ball mill or any other type of equipment useful for grinding or pulverizing hard resin fragments into fine particles. The extent of subdivision is determined primarily by practical consideration as is necessary to be compatible with the intended purpose of the paper. Thus, in the photographic field, the major application of the invention, the particle size should be such as to permit uniform incorporation in the formulation to be coated on the paper without disrupting or otherwise disturbing the continuity or the surface quality of the finishing coating. For example, particles of a size causing the coating to have a perceptibly roughened or irregular surface would be poorly adapted, if at all, for photographic materials. In general, a particle size of about $\frac{1}{10}$ to 1 micron will be acceptable with a size in the same order as that of the usual pigments mentioned above, say about ½ micron being preferred.

The following are the structural formulae of the known optical bleaching agents that have been found useful in the practice of the present invention, although it will be appreciated that others having comparable chemical properties may well exist and could be substituted with generally similar effect:

(1)



(2)



Methods of preparing compounds having the above formulae are described in the following publications, the order of numbering corresponding to the list above:

(1) Chem. Abs. B44 (1950), p. 2251
(2) Org. Synth. Coll., vol. II, p. 231

For carrying out the process according to the present invention, the desired amount of the finely divided urea-formaldehyde resin is dispersed in an excess of water. To this suspension is added a solution of the optical bleaching agent involved. If the optical bleaching agent is not or not sufficiently soluble, it can likewise be added in dispersed form to the suspension. Absorption of the optical bleaching agent is preferably facilitated by heating the suspension to a temperature between about 50 and 100° C., the treatment being continued until no more fluorescing substance is bound. The time required to achieve this condition will ordinarily range between about 30–60 minutes, depending upon the temperature. The mixture is then filtered under suction, leaving a strongly fluorescing paste which strongly retains the fluorescing substance and which can be added to the coating composition to be applied to a paper support. Thus, the fluorescing mass can, for instance, be added to a silver halide photographic emulsion composition which is spread upon a paper after applying the baryta-coating composition thereto. While preliminary treatment of the finely divided polyamide with the optical bleaching agent is usually best, where experience has indicated the amount of a particular agent that can be expected to be bound to a given amount of resin, the treatment can often be effected in situ by admixing the amount of agent and amount of resin directly to the coating formulation. In this case, the heat applied to dry the coating will serve to promote the combination of the agent and resin.

The proportion of the treated urea-formaldehyde resin needed in the coating formulation to achieve the advantages of the invention can be adjusted to meet the requirements of any particular paper and/or surface coatings. Obviously, any amount will contribute a proportionate effect and will improve the performance of the paper to that extent. As a general rule, about 5 to 25% by weight of the coating in which the resin is employed, the photographic emulsion coating, for example, will suffice.

Our experiments to date have not clearly revealed the exact mechanism by which the optical bleaching agent becomes bound to the resin. Presumably, physical or chemical forces or a combination of the two are involved but the invention is not to be restricted to any particular theory.

The wandering of the optical bleaching agent out of the layer in which it was applied is practically completely precluded by the method of the present invention, so that the exposed photographic element after complete processing, which even may include a protracted rinsing step, yields a photographic image characterized by strongly brightened white areas.

The present invention is further illustrated in the fol-

lowing example without limiting, however, the scope thereof.

In the examples, the formula number given in parenthesis corresponds to the number in the list of structural formulae set forth previously.

Example 1

1 kg. of a urea-formaldehyde resin prepared according to Example I of Belgian specification 451,470 having a particle size of about ½ micron is dispersed in 3000 cc. of water together with 10 gm. of 1,2-di(5-methylbenzimidazyl-2)-ethylene (Formula 1). The solids are kept in suspension by strong stirring for 30 minutes at a temperature of about 60° C. At the end of this time, the solids are recovered by filtering under suction or centrifugation 50 gm. of the resultant treated resin particles are added to 1 kg. of a photographic silver halide emulsion composition which is then coated in the usual way on a paper support. The paper thus obtained could be reused without apparent loss in the whiteness of its surface color. After exposure and conventional development, the photographic image on the paper is strongly brightened in the white areas thereof.

A similar result is obtained when the procedure above is repeated using the urea-formaldehyde of Example II of the Belgian patent.

Example 2

1 kg. of a urea-formaldehyde resin prepared according to the method indicated in Example I of the Belgian patent is suspended in 3000 cc. of water. To the suspension are added 1000 cc. of a 1% ethanol solution of 4,5-diphenylimidazalone-2 (Formula 2). The mixture is kept in suspension by strong stirring for 30 minutes at a temperature of about 60° C. Then, the solids are recovered by filtering under suction. The resultant treated particles are added to a photographic emulsion and processed as described in Example I with comparable results.

The above procedure is repeated using the resin prepared according to Example II of the Belgian patent without significant difference in the results obtained.

We claim:

1. A light-sensitive photographic paper comprising a paper support, a white pigmented coating on a surface of said support, and a superposed light-sensitive silver halide emulsion layer, said emulsion layer containing discrete fluorescent particles obtained by heating an aqueous suspension of a finely-divided, water-swellable, water-insoluble, urea-formaldehyde resin, through which suspension is uniformly distributed an optical brightening agent selected from the group consisting of:

(1) 1,2-di(5-methylbenzimidazolyl-2)-ethylene,

(2) 4,5-diphenylimidazolone-2.

2. A paper according to claim 1 wherein said fluorescent mass constituted about 5 to 25% by weight of said emulsion layer.

3. A paper as in claim 1 wherein urea-formaldehyde resin has a particle size not greater than about 1 micron.

4. A duplication paper of the type employed in photographic and transfer processes, comprising a paper support and a silver halide emulsion layer carried by said paper support, said emulsion layer containing discrete fluorescent particles obtained by heating an aqueous suspension of a finely-divided, water-swellable, water-insoluble, urea-formaldehyde resin, through which suspension is uniformly distributed an optical brightening agent selected from the group consisting of:

(1) 1,2-di(5-methylbenzimidazolyl-2)-ethylene,,

(2) 4,5-diphenylimidazolone-2.

5. A method of enhancing the surface whiteness of a paper having at least one surface coating of a silver halide emulsion, which method comprises incorporating into said coating discrete fluorescent particles obtained by heating an aqueous suspension of a finely-divided, water-swellable, water-insoluble, urea-formaldehyde resin, through which suspension is uniformly distributed an optical brightening agent selected from the group consisting of:

(1) 1,2-di(5-methylbenzimidazolyl-2)-ethylene,,

(2) 4,5-diphenylimidazolone-2.

6. The paper of claim 1 wherein said resin is prepared in the presence of an alkaline polymerization catalyst.

7. The paper of claim 4 wherein said resin is prepared in the presence of an alkaline polymerization catalyst.

8. The method of claim 5 wherein said resin is prepared in the presence of an alkaline polymerization catalyst.

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NORMAN G. TORCHIN, *Primary Examiner.*

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,181,950

May 4, 1965

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It is hereby certified that error appears in the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

In the heading to the printed specification, line 13, for "June 6, 1967" read -- June 6, 1957 --.

Signed and sealed this 30th day of November 1965.

(SEAL)
Attest:

ERNEST W. SWIDER
Attesting Officer

EDWARD J. BRENNER
Commissioner of Patents