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SILVER HALIDE EMULSIONS FOR BLACK AND WHITE PRINTS CONTAINING BRIGHTENING AGENTS

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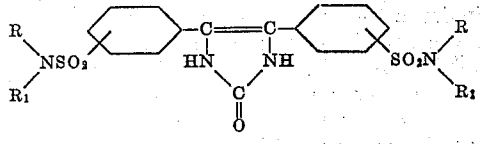
6 Claims. (Cl. 95—7)

The present invention relates to photographic emulsions and particularly to sliver halide emulsions for black and white prints containing a condensation product of 4,5-diphenylglyoxalonedisulfonyl chloride with an organic amine as a brightener of the white portions of the silver image formed after exposure and development of said emulsion.

The white portions in most black and white photographic prints regardless of the nature and constitution of the base material possess a grayish or yellowish cast or tint. This cast is more pronounced after the print has been stored for some time, even in the absence of natural or artificial light. The cast or tint is probably due to the degradation products of the photographic developer formed during development of the silver image.

It is known that many organic compounds known as brightening agents are utilized for the treatment of textiles to impart an overall whitening in bright light. Brightening agents of the stilbene type are currently utilized for this purpose and affect textiles uniformly causing a whitening of each portion thereof. Cellulosic derivatives usually have a yellowish tint and in order to counteract the undesirable tint, brightening agents, particularly spirit-soluble safranine, are incorporated into the cellulosic derivative or in a bonding layer which is coated over the derivative or between two sheets of the cellulosic derivative.

Inasmuch as practically all of the brightening agents cause the fabrics and cellulosic derivatives to which they are applied to assume an overall whiteness, considerable difficulty ws encountered in solving the foregoing photographic problem. Most of the currently used brightening agents when applied to photographic images produce not only a brightening of the white areas but also a whitening of the shadowy dark areas. Similarly, it applied to color film, the brightening agents not only affect the white portions of the images, but the colored portions as well. We have discovered that a certain class of brightening agents, when incorporated into silver halide emulsions for producing black and white images upon exposure and developement of the silver halide, operate very noticeably on the white portions of the black and white images, thus causing a noticeable increase in contrast. Such compounds are products obtained by the condensation of 4,5-diphenylglyoxalonedisulfonyl chloride with an organic amine and are characterized by the following general formula:



wherein R represents hydrogen, an aliphatic, aromatic, or heterocyclic radical and R_1 represents an aliphatic, aromatic, or heterocyclic radical, R and R_1 including an alkyl group of at least six carbon atoms and a solubilizing group, such as carboxylic or sulfonic acid group.

The compounds characterized by the foregoing general formula are readily prepared by condensing one molecular proportion of 4,5-diphenylglyoxalonedisulfonyl chloride with at least two molecular proportions of a primary or secondary aliphatic, aromatic, or heterocyclic amine, containing an alkyl chain of at least six carbon atoms and a solubilizing group, such as sulfonic or carboxylic acid.

The 4,5-diphenylglyoxalonedisulfonyl chloride is dissolved in a sufficient volume of anhydrous pyridine and added to a mixture of the amine which is also dissolved in anhydrous pyridine and to the mixture a small quantity of anhydrous sodium aceate is added, and the mixture heated at the temperature of steam for about five to seven hours. After cooling, the solid product is isolated by recrystallization from hot water.

The unusual feature of the foregoing condensation reaction is that any primary or secondary aliphatic, aromatic, or heterocyclic amine will condense with the 4,5-diphenylglyoxalonedisulfonyl chloride under the aforestated conditions to produce compounds corresponding to the above formula. However, for purposes of this invention, it is essential that the amine, whether primary or secondary, aliphatic, aromatic, or heterocyclic, contain as a substituent both an alkyl chain of at least six carbon atoms and a water solubilizing group, such as carboxylic or sulfonic acid. The inclusion of the alkyl chain of at least six carbon atoms imparts non-diffusing properties to the compound and the water solubilizing group permits moderate solubility in water for incorporation into silver halide emulsions.

The various amines which may be condensed with 4,5-diphenylglyoxalonedisulfonyl chloride are legion and no difficulty will be encountered in selecting the proper one so as to yield the desired product. As illustrative examples of such amines, the following may be mentioned:

AROMATIC

1 - amino - 4 - methyloctadecyl - aminobenzene-3-sulfonic acid.
1-amino-4-dodecylaminobenzene-3-carboxylic acid.
1 - amino - 4 - perhydrodiphenylaminobenzene-3-carboxylic acid.
1-amino-2-oleylaminobenzene-5-sulfonic acid.
1 - amino - 2 - methyloctadecylaminobenzene-3-carboxylic acid.
1-amino-2-dodecylaminobenzene-3-sulfonic acid.
6-tetradecylamino metanilic acid.
6-cetylamino metanilic acid.
6-octadecylamino metanilic acid.
6-myristoylamino-2-toluidine-4-sulfonic acid.
6-palmitoylamino-2-toluidine-4-sulfonic acid.
6-stearoylamino-2-toluidine-4-sulfonic acid.
6-(N-methyl-N-tetradecanoylamino)-metanilic acid.
6-(N-methyl-N-octadecanoylamino)-metanilic acid.
6-(N-ethyl-N-tetradecanoylamino)-metanilic acid.
6-(N-ethyl-N-cetanoylamino)-metanilic acid.
6-(N-ethyl-N-octadecanoylamino)-metanilic acid.

HETEROCYCLIC

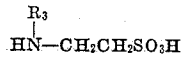
1-tetradecyl-2-(4-aminophenyl)-benzimidazole-5-sulfonic acid.
1-cetyl-2-(4-aminophenyl)-benzimidazole-5-sulfonic acid.
1-octadecyl-2-(4-aminophenyl)-benzimidazole - 5-sulfonic acid.

ALIPHATIC

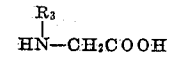
N-tetradecyl taurine.
N-cetyl taurine.
N-octadecyl taurine.
N-tetradecyl glycine.
N-cetyl glycine.
N-octadecyl glycine.

It is to be clearly understood that the configuration or structure of the aliphatic, aromatic, and heterocyclic amine, whether primary or secondary, is immaterial so long as it contains an alkyl substituent in any part of the molecule of at least six carbon atoms and a water solubilizing group. These amines may be further characterized by the following formulae:

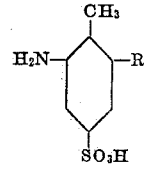
ALIPHATIC



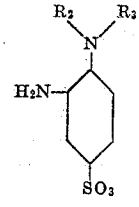
and



AROMATIC

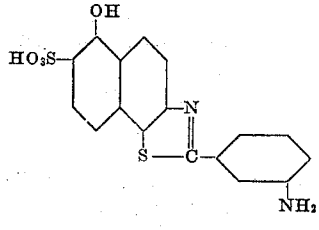


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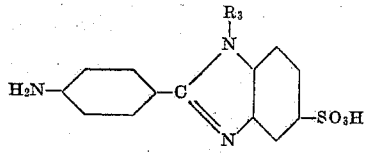


HETEROCYCLIC

German Patent 165,126



and



wherein R_2 represents hydrogen or a lower alky., such as methyl, ethyl, propyl, butyl, etc., and R_3 represents an alkyl chain of at least six carbon atoms, such as hexyl, heptyl, octyl, nonyl, decyl, dodecyl, tridecyl, tetradecyl, pentadecyl, heptadecyl cetyl, octadecyl, and the like.

The brightening compounds characterized by the above general formula are incorporated into any type of silver halide emulsion employed in the manufacture of photographic contact and projection paper.

In the preparation of silver halide emulsion whether a single silver halide salt or a mixture of silver halides, such as chlorobromides, bromoiodides, or chlorobromoiodides, the brightening agents per se in finely divided form or a solution thereof in water or an alcohol-water mixture is made and the powdery form or a solution thereof is mixed with the emulsion at any point during its preparation, i. e., ripening, curing, or settling stage, but preferably during ripening or just prior to coating. The concentration of the brightening agent incorporated into the silver halide emulsion may be any amount which will brighten the white portions of the print after exposure and development of the emulsion. Brightening amounts may

range from about 0.05 to 10 grams per liter of emulsion to yield satisfactory results. The amount added is not critical and perceptible results are obtained with quantities below 50 milligrams per liter of any type of emulsion. Increasing the amount beyond 10 grams per liter serves no useful purpose and may have a yellowing effect.

The actual concentration employed will depend upon the type of emulsion used and varies slightly with the brightening agent employed, and the brightening amount to be actually employed can be very readily determined by simple routine tests. In case a water or alcohol-water solution is employed, it is best prepared by dissolving the brightening agent in the smallest amount of solvent necessary to effect solution and the solution added with stirring to a silver halide emulsion so that the final volume of the silver halide emulsion will be one liter.

When applied within the stated proportions to silver halide emulsions, the white portions of the prints after exposure and development are considerably whiter with a considerable increase in the contrast when compared to a control black and white print. When applied to color prints, very little brightening is observed. In fact, a tonal change may be brought out in the blue and magenta layers. The unusual feature of the brightening agents utilized in accordance with the present invention is that since they are substantive to photographic colloids, such as gelatin, polyvinyl alcohol, and the various gelatin substitutes, they are not readily removed during the development and washing steps of the exposed print and are retained in the colloid layer indefinitely and enhance the brightness of the white areas of the photographic images.

The colloidal carrier for the silver halide emulsion may be gelatin, water soluble cellulose derivatives, such as hydroxylethylcellulose, methylcellulose, carboxymethylcellulose, low acetyl value cellulose, polyvinyl alcohol, partially hydrolyzed polyvinyl acetate, acetals of polyvinyl alcohol, partially hydrolyzed vinyl acetate-ethylene copolymers, and the like. A surface active agent, such as sulfated oleic acid, alkylated monosodium benzenesulfonate, dihexyl ester of sodium sulfosuccinate, sodium salt of an alkylnaphthalene sulfonic acid, sodium salt of tetrahydronaphthalene sulfonic acid, calcium glycerin phosphate, alkylphenyl-polyethylene glycol, oleic acid ester of hydroxyethane sulfonic acid, and sulfonates of high molecular weight primary or secondary aliphatic, aromatic, and cycloalipahtic carboxy acids, may be added to effect a smoother coating. It is to be noted, however, that any commercially available surface active agent may be employed. The nature of the surface active agent is immaterial so long as it possesses wetting, dispersing, and emulsifying properties, and its aqueous solutions are colorless or only slightly tinted.

The black and white photographic material may be either a contact printing paper, a projection printing paper, ordinary black and white film, which may be a positive or negative, or motion picture film. The addition products whether incorporated in the silver halide emulsion layer or as a supercoating over the emulsion layer are substantive to gelatin and other water permeable colloids, and as a consequence, non-diffusing in photographic processing baths.

The base material, i. e., support for the silver halide emulsion may be the usual baryta paper, white opaque cellulose acetate, and the like. In fact, the nature or constitution of the base is immaterial since the effect is in the white portions of the silver image.

Another unusual feature of the brightening agents utilized in accordance with the present invention is that they may also be employed in the pigmenting layer of a photographic paper or white opaque cellulose acetate to enhance the brightness of the white areas of the photographic image in the overcoated colloid layer. The photographic paper or white opaque cellulose acetate is coated with a layer of pigment, such as barium sulfate.

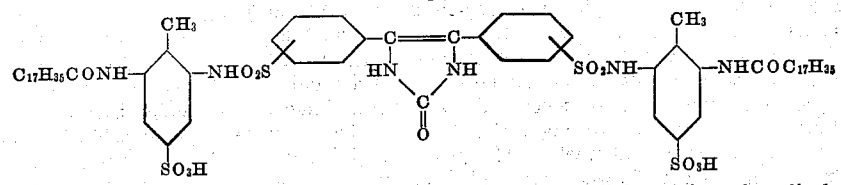
titanium dioxide, calcium carbonate, calcium sulfate, feldspar, fluorspar, neutral calcium phosphate, and the like, dispersed in the same colloid carrier which is utilized for carrying the silver halide emulsion as described above. The percentage of the pigmenting agent may be that ordinarily employed in the case of gelatin baryta coatings and is well known in the art. In this application, the brightening agents are employed in a concentration ranging from 0.1 gram to 15 grams per liter of a water dispersion of the colloid carrier and pigmenting agent. The dispersion is spread upon the paper or white opaque cellulose acetate in a thin coating. Upon evaporation of the water, a pigmented colloid layer is obtained. The light sensitive photographic paper or white opaque cellulose acetate is then formed by applying a silver halide photographic emulsion layer to the pigmented layer in the usual manner.

Despite the fact that the brightening agents are moderately soluble in water, they do not, however, form any quantitative amount of insoluble salts when in contact with any one of the pigmenting agents. The very small amount of water insoluble salt that may be formed will not affect the brightening agents' substantivity to the colloid carrier.

The method of testing the effect in silver halide emulsions consists merely of coating a film or paper support with the same emulsion, one with and one without the brightening agent, exposing and developing the film or paper, and then storing it for a period of three to six months either in a closed container or in a photograph album that is exposed to the atmosphere. The change in color, i. e., cast or tint, of the silver image in the picture area in the two emulsions is then observed and found in all cases to be less in the emulsions containing brighteners.

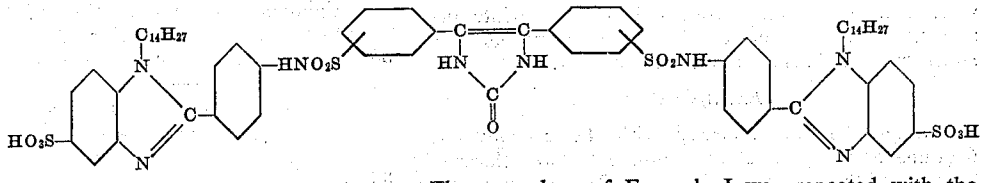
The invention is further illustrated by the following examples, but it is to be understood that the invention is not limited thereto. All the parts are given as parts by weight unless otherwise specified.

Example I



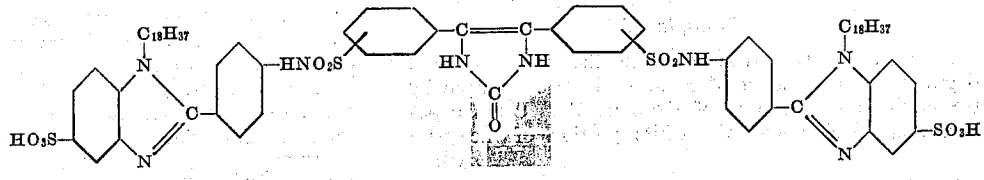
A mixture of 108 parts of 4,5-diphenylglyoxalonedisulfonyl chloride in 1300 parts of anhydrous pyridine was added to a mixture of 352 parts of 6-stearoylamino-2-toluidine-4-sulfonic acid in 1700 parts of anhydrous pyridine. 41 parts of anhydrous sodium acetate were added and the mixture heated at the temperature of steam for six hours. After cooling, the solid product was isolated in the usual manner by recrystalliaztion from hot water.

Example II



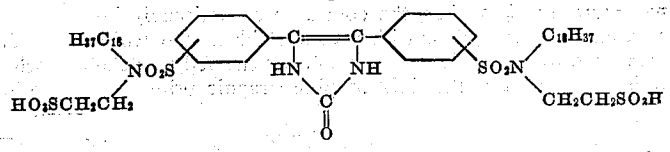
The procedure of Example I was repeated with the exception that 335 parts of 1-tetradecyl-2-(4-aminophenyl)-benzimidazole-5-sulfonic acid were used in place of 352 parts of 6-stearoylamino-2-toluidine-4-sulfonic acid.

Example III



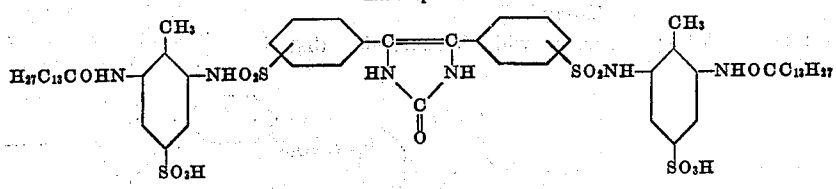
The procedure of Example I was repeated with the exception that 406 parts of 1-octadecyl-2-(4-aminophenyl)-benzimidazole-5-sulfonic acid were used in place of 352 parts of 6-stearoylamino-2-toluidine-4-sulfonic acid.

Example IV



The procedure of Example I was repeated with the exception that 283 parts of N-octadecyl taurine were used in place of 352 parts of 6-stearoylamino-2-toluidine-4-sulfonic acid.

Example V



The procedure of Example I was again repeated with the exception that 309 parts of 6-myristoylamino-2-

toluidine-4-sulfonic acid were used in place of 352 parts of 6-stearoylamino-2-toluidine-4-sulfonic acid.

Example VI

To a gelatin silver chlorobromide emulsion of normal speed and contrast, 6 grams of the product of Example I dissolved in 250 cc. of hot water were added with stirring and the solution made up to volume, i. e., one liter. After the brightening agent was thoroughly dispersed in the emulsion, the emulsion was coated upon a subbed paper base, allowed to dry, and then exposed and developed to a silver image. Another paper base coated with the same emulsion but containing no brightening agent was exposed and developed to a silver image. Both prints were placed upon a laboratory shelf and examined after several weeks. The print containing the brightening agent showed remarkable improvement in brightness, i. e., the white portions were definitely a bright white color, whereas the print which contained no brightening agent showed a considerable yellowish cast.

Example VII

Example VI was repeated with the exception that 6 grams of the product of Example I were replaced by 8 grams of the product of Example II. Upon exposure and development, the white portion of the print was considerably whiter, the contrast was noticeably increased when compared with a control black and white print, and the whitening agent employed showed no deleterious effect upon the finished photographic print.

Example VIII

Example VI was repeated with the exception that 6 grams of the product of Example I were released by 2 grams of the product of Example III. Upon exposure and development, the white portion of the print was considerably whiter, the contrast was noticeably increased when compared with a control black and white print, and the whitening agent employed showed no deleterious effect upon the finished photographic print.

Example IX

Example VI was repeated with the exception that 6 grams of the product of Example I were replaced by 0.5 gram of the product of Example IV. Upon exposure and development, the white portion of the print was considerably whiter, the contrast was noticeably increased when compared with a control black and white print, and the whitening agent employed showed no deleterious effect upon the finished photographic print.

Example X

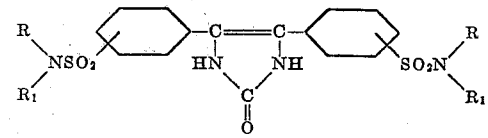
Example VI was repeated with the exception that 6 grams of the product of Example I were replaced by 1 gram of the product of Example V. Upon exposure and development, the white portion of the print was considerably whiter, the contrast was noticeably increased when compared with a control black and white print, and the whitening agent employed showed no deleterious effect upon the finished photographic print.

Silver halide emulsions containing the brightening agents of the present invention have the added advantage in that the agents do not influence the speed of the contrast of the unexposed emulsion while in package form and storage. The brightening agents may be used on various kinds of silver halide emulsions. In addition to being useful in silver chloride emulsions, they may be used in chloride, bromide, bromoiodide, and chlorobromoiodide emulsions. They are equally useful in sensitized and unsensitized emulsions, boil type, ammonia type, and paper emulsions of various types.

Various modifications of this invention will occur to those skilled in the art and it is, therefore, understood that the invention is limited only by the scope of the appended claims.

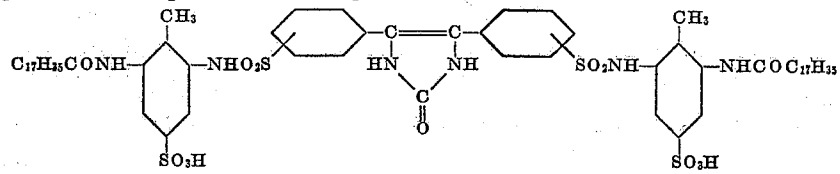
We claim:

1. A light sensitive photographic emulsion for forming black and white images therein comprising a support and a light sensitive silver halide emulsion layer containing, in a brightening amount, a brightening agent capable of brightening the white portions of the silver image formed after exposure and development of said emulsion, characterized by the following general formula:

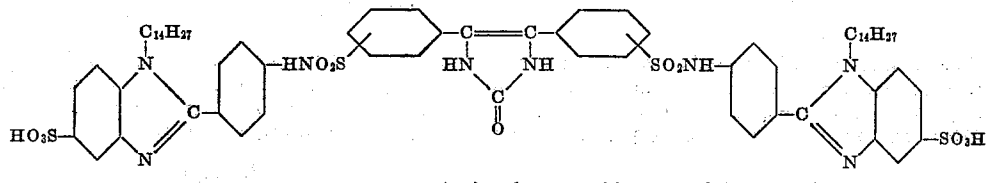


wherein R represents a member selected from the class consisting of hydrogen, aliphatic, aromatic, and heterocyclic radicals, R_1 represents an aliphatic, aromatic, or heterocyclic radical, one of said radicals consisting of R and R_1 containing an alkyl group of at least six carbon atoms and a water solubilizing group selected from the class consisting of carboxylic and sulfonic.

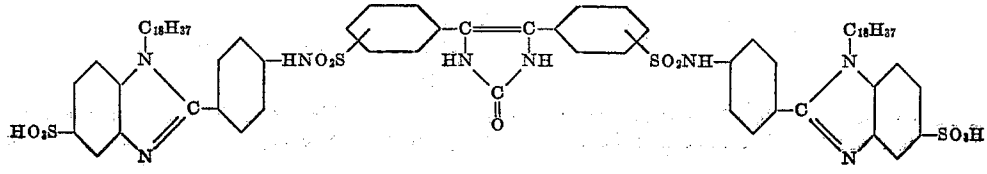
2. A photographic material according to claim 1, wherein the brightening agent is characterized by the following formula:



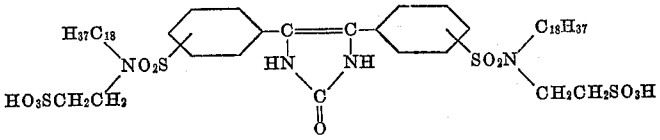
3. A photographic material according to claim 1, wherein the brightening agent is characterized by the following formula:



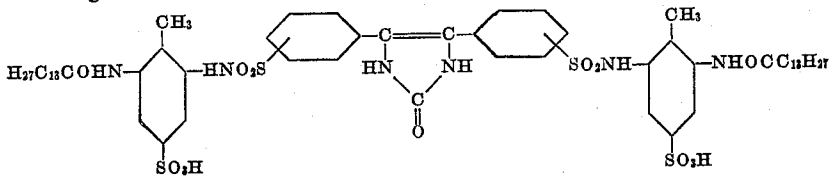
4. A photographic material according to claim 1, wherein the brightening agent is characterized by the following formula:



5. A photographic material according to claim 1, wherein the brightening agent is characterized by the following formula:



6. A photographic material according to claim 1, wherein the brightening agent is characterized by the following formula:



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