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UNITED STATES PATENT OFFICE

2,545,423

DIAZOTYPES CONTAINING A GUANIDE BASE IN A GELATIN LAYER TO PREVENT DYE DIFFUSION

Herman H. Duerr, Binghamton, N. Y., assignor to General Aniline & Film Corporation, New York, N. Y., a corporation of Delaware

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4 Claims. (Cl. 95—8)

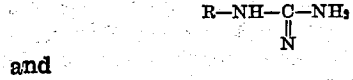
1

The present invention relates to the manufacture of improved sensitive papers for the production of photographic images by the diazo type process.

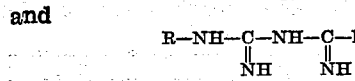
The diazo type process consists of exposing beneath a pattern a light sensitive layer containing a light sensitive diazo compound and a coupling compound on a suitable supporting medium, such as paper, whereby the said diazo compound is decomposed where unprotected by the outlines of the pattern and its ability to combine with an azo dye coupling component is destroyed. After exposure, development is effected by bringing the exposed layer into contact with gaseous ammonia to cause coupling of the undestroyed diazo compound and the coupling component. A replica of the original design is obtained as an azo dye image on light ground. This is known as the dry developing process and the sensitive material employed in the process is known as the dry print paper.

The sensitive (dry print) paper is prepared with a solution containing both the diazo compound and the coupling component on a suitable carrier, such as textiles, paper, cellulosic films, and the like. The dyestuff components, as applied on the carrier, are relatively unstable and cannot be stored for long periods of time prior to use, especially under conditions of high humidity. The diazo compound and the coupling component of the sensitized composition tend to diffuse into the carrier layer, and in the case of a paper base, into the underlying baryta coating or into the paper fiber. As a consequence of this diffusion, the paper after exposure and development shows a mottled effect.

I have found that the foregoing shortcomings can be obviated by interposing between the light sensitive layer and the carrier layer, a gelatin layer or other colloid layer containing a guanide or biguanide base, characterized by the following general formulae:



and

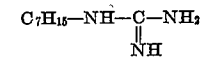


wherein R is an alkyl, aralkyl or acyl group of at least 7 carbon atoms, e. g., heptyl, octyl, nonyl, decyl, undecyl, dodecyl, tridecyl, tetradecyl, pentadecyl, hexadecyl, heptadecyl, octadecyl, and the like, benzyl, phenylethyl, phenylpropyl, phenylisopropyl, phenylbutyl, etc., benzoyl, octanoyl, palmitoyl, cinnamoyl, cumoyl, oleoyl, xyloyl, naphthoyl, stearoyl, and the like.

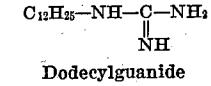
The above bases, wherein R is an alkyl or aralkyl group, are prepared from their inorganic salts described in United States Patent 2,149,709 by rendering an aqueous solution of such salt alkaline with sodium hydroxide, potassium, hydroxide, or sodium carbonate and extracting the precipitate with a solvent such as ether, toluene or benzene. Where R is an acyl group, such bases are prepared in the manner from the salts described in British Patent 546,027.

2

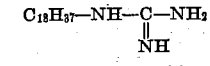
The following are examples of the guanide and biguanide bases, which for the sake of convenience and brevity will be referred to hereinafter as guanide bases prepared in accordance with the methods in the above patents:

(1) 

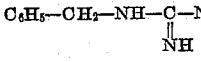
Heptylguanide

(2) 

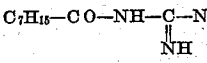
Dodecylguanide

(3) 

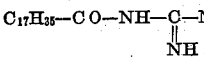
Octadecylguanide

(4) 

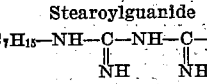
Benzylguanide

(5) 

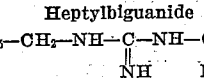
Caprylylguanide

(6) 

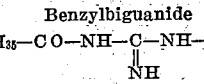
Stearoylguanide

(7) 

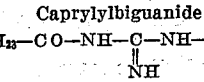
Heptylbiguanide

(8) 

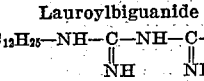
Benzylbiguanide

(9) 

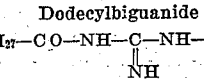
Caprylylbiguanide

(10) 

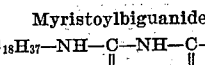
Lauroylbiguanide

(11) 

Dodecylbiguanide

(12) 

Myristoylbiguanide

(13) 

Octadecylbiguanide

The above guanide bases are dispersed in the form of the alcoholic solutions in a 1.0% to 7% aqueous solution or dispersion of gelatin or other

colloid in an amount ranging from 1 to 15 grams per liter of solution or dispersion and then coated upon the carrier base, such as opaque paper, paper coated with baryta, transparentized paper, cellulose acetate film, textile cloth, fiber board, or other suitable carrier base normally employed in this art. The gelatin or colloid coating, containing the guanide base, is applied to the carrier base to a dry thickness of about 3–6 mμ. Over this layer is then coated the usual diazo-type two-component light sensitive coating composition.

By this simple expedient, the intermediate gelatin or colloid layer acts as a barrier between the base and light sensitive coating composition and precludes the dyestuff components in said composition from migrating or diffusing into the carrier base. This markedly overcomes the tendency to form stain and the mottle effect after exposure and development of the material.

Either one of the diazo compounds or the coupling components, both of which constitute the dyestuff coating composition must contain a sulfonic, carboxylic, or acid sulfate group. These groups should be preferably in the coupling position of the dye coupling component which is split off during dye coupling in the developing process.

When the gelatin or colloid coating has been interposed between the carrier base and light sensitive layer, the diazo compound or the coupling component or both, containing either sulfonic, carboxylic, or acid sulfate groups, which have migrated to the gelatin coating layer will form insoluble salts with the guanide base and are thus prevented from diffusing into the carrier base. Due to the fact that said acid groups of the coupling component form a very insoluble salt, the groups are precluded from splitting off during dye coupling. The precipitated diazo compound or coupling component, or both, at the boundary between the gelatin barrier layer and the light sensitive layer forms a further barrier which completely prevents the diffusion of the dyestuff components in the light sensitive layer into the base.

Although this invention will be particularly described as applied to the two-component diazo-type process, it is to be understood that it can be applied to the one-component process or moist, or as it is usually called a semi-dry, developing process. In this process, the printing paper is prepared with a solution containing the diazo-body only (generally in the presence of an acid or acid salts). For the developing of this paper, a liquid developer containing in addition to the alkali, also the coupling component, is applied over the diazo-body coating in a thin layer.

As examples of diazo compounds which are used in the preparation of the two-component light sensitive layer and are in the form of their stabilized salts, such as the $ZnCl_2$, $CdCl_2$, or $SnCl_4$ double salts, fluorborates, aryl or alkyl sulfonates, and acid sulfates of the diazonium compound, those derived from p-diamines of the benzene series, particularly those in which one of the amino groups is substituted by such groups as alkyl, alkoxyalkyl, aryl, aralkyl, alkylol, cycloaliphatic, and heterocyclic groups may be employed. Examples of such amines are N-hydroxyethyl - N - methylamino - p - amino - benzene, p-amino diphenylamine, 1-monoethylamino-2-(or 3-) methyl-4-amino-benzene, 1-N-hydroxyethyl-N-ethylamino-3-methyl-4-amino-benzene, 1-diethylamino-3-ethoxy-4-amino-benzene, 4-amino-1-benzoylamino-2,5-diethoxy-benzene, p-amino-N-diethylaniline, 1-N,N-di(hydroxyethyl) amino-3-chloro-4-amino-benzene, p-amino-N-ethyl-N-benzylaniline, p-amino - N - dimethylaniline, 1-ethylamino-4-amino-benzene, 1-hydroxy-ethyl-ethylamino-4-amino - benzene, p-phenylene-diamine, 4-amino-N,N-dioxyalkylaniline and 4'-ethoxyphenyl-2,5-diethoxyaniline.

Dye coupling components which may be utilized are legion and well known to those skilled in the art, and hence an extensive listing of them need not be made herein. It will suffice to say that compounds of this type comprise phloroglucin, H-acid, β-naphthol, resorcin, 1-naphthol-3,8-disulfonic acid, 1-amino-8-naphthol-3,6-disulfonic acid, and the like.

The following specific examples illustrate several of the various methods of preparing the gelatin barrier layers and it will be understood that these examples merely represent the preferred embodiments and are not to be considered as limitative.

Example I

10 cc. of a 5% solution of dodecylguanide in methanol were dispersed in 500 cc. of a 1.5% aqueous solution of gelatin and the resulting solution coated on a baryta coated paper to a dry thickness of approximately 3–4 mμ by the usual coating method. Over this gelatin layer then was coated the usual light sensitive layer consisting of a solution of the diazo compound p-phenyleneaminobenzene diazonium acid sulfate, and a coupling component 2,3-dihydroxynaphthalene.

Example II

10 cc. of a 10% solution of heptylguanide in ethanol were dispersed in 500 cc. of a 5% aqueous solution of gelatin and the resulting solution coated on a paper base to a dry thickness of approximately 4 mμ by the usual coating method. Over this gelatin layer there was coated the usual light sensitive layer consisting of a solution of a zinc chloride double salt of the diazo compound obtained from N-ethonal-ethylamino-4-aminobenzene and as a coupling component R-acid (β-naphthol-3,6-disulfonic acid).

Example III

100 cc. of a 10% solution of stearoyl biguanide in methanol were dispersed in an 8% aqueous gelatin solution containing .5% alum. This solution was used for top sizing of the raw print paper on a paper-making machine. Over this gelatin top sizing layer there was coated the usual light-sensitive layer consisting of a solution of a diazo compound 2,1-diazo-hydroxy naphthalene-5-sulfonic acid, and as a coupling compound, J-acid (2,5-amino naphthol-7-mono-sulfonic acid).

The light sensitive layers prepared according to the above examples did not show any stain or mottled effect after processing. This was due to the fact that both dyestuff components failed to diffuse into the base so that no dye was formed therein during development.

It is obvious from the description and examples that many modifications can be made without departing from the spirit of the invention. Instead of gelatin other colloids such as starch, casein, water-soluble cellulose derivatives, e. g., hydroxyethyl cellulose, methyl cellulose, low acetyl value cellulose acetate; mixture of gelatin with a polyamide as described in United States

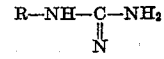
Patent 2,289,775; polyvinyl alcohol and gelling agents as described in United States Patent 2,249,537; polyvinyl acetaldehyde acetal resins and partially hydrolyzed acetate resins described in United States Patents 1,939,422 and 2,036,092, and the like, may be employed as dispersing mediums for the guanide bases, and such solutions or dispersions utilized as coatings upon the carrier base or as sizing which is applied to the paper web during the paper making operation. In lieu of the latter, the colloid dispersion of the guanide base may be utilized for top sizing of the finished paper base.

By the term "carrier" as used herein and in the appended claims, I mean the various materials which have been and are currently used for carrying the light sensitive material. In the art as presently developed, these materials comprise paper or vegetable fibers which may be either transparent, translucent, or opaque. Cloth and films of cellulose nitrate, cellulose acetate, regenerated cellulose, gelatin and the like may be employed. Inasmuch as there is no chemical coaction between the carrier and the gelatin or other colloid barrier layer, the nature or constitution of the carrier base is immaterial.

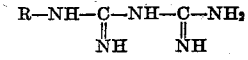
I claim:

1. A light sensitive printing material for use in the production of diazotype prints comprising a base coated with a gelatin layer and a superimposed light sensitive coating comprising a diazo compound and an azo coupling component, at least one of which contains an acid group, and

said gelatin layer containing dispersed therein a guanide base of the class consisting of the bases having the following general formulae:



and



wherein R represents a member of the class consisting of alkyl, aralkyl, and acyl groups of at least 7 carbon atoms.

2. A light sensitive printing material according to claim 1 wherein the guanide base is dodecylguanide.

3. A light sensitive printing material according to claim 1 wherein the guanide base is heptylbiguanide.

4. A light sensitive printing material according to claim 1 wherein the guanide base is stearoylbiguanide.

HERMAN H. DUERR.

REFERENCES CITED

The following references are of record in the file of this patent:

UNITED STATES PATENTS

Number	Name	Date
1,807,761	Sprongerts	June 2, 1931
1,822,065	Sprongerts et al.	Sept. 8, 1931
2,418,623	Chechak	Apr. 8, 1947