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LIGHT-SENSITIVE DIAZOTYPE LAYERS CONTAINING CARBOXAMIDES

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This invention relates to an improvement in the production of photographic prints by the diazotype process and more particularly to the manufacture of improved light-sensitive materials for the production of photographic images by the diazo process.

Light-sensitive dry print materials used in the diazotype process are prepared by impregnating or coating a suitable base, such as paper or similar absorbent, fibrous supports, with a solution containing a light-sensitive diazo compound and an azo coupling component. For the reason that the dyestuff components, as coated on the carrier, are relatively unstable and in order to prevent coupling prior to alkaline development, the coating solution also usually contains small amounts of an acid such as citric acid, tartaric acid, tricarballylic acid, phosphoric acid and the like, and a stabilizing or anti-oxidizing agent such as thiourea, allyl isothiocyanate and the like, which prevents background discoloration on the finished print. Another important ingredient of diazo materials is zinc chloride which acts not only as a hygroscopic agent but also improves the keeping quality of the coated unexposed paper under adverse storage conditions, especially those of high humidity or of dry heat.

The sensitive dry print material is exposed to ultraviolet light through a suitable pattern, for instance, a line drawing or a photographic transparency. The diazo compound is decomposed by the action of light where it is unprotected by the pattern of light and its ability to combine later with the coupling component is destroyed. The exposed layer is subsequently developed by bringing it in contact with ammonia vapors, thereby causing the coupling of the undestroyed diazo compound and the coupling component. A reproduction of the original pattern is obtained as an azo dye image on a light background.

This procedure, known as the dry developing process, is carried out with automatic printing and processing equipment which performs successively the two operations of exposure and dry development by transporting the print material with the same speed through separate exposure and development chambers.

The overall speed of the commercially available diazotype processing equipment can generally be varied between the limits of one foot and thirty feet per minute but does not permit any automatic differentiation between the speed of travel in the exposure and the development chambers. In order to achieve their maximum possible output, these printers are usually operated at, or near, their maximum speed. This increased rate of travel through the developer chamber often yields badly underdeveloped prints which not only have unsatisfactorily low dye densities but also display poor storage characteristics. Moreover, such incompletely developed prints tend to bleach out seriously if left even in ordinary room light, presumably as a consequence of the decomposition of the uncoupled diazonium salt.

Various remedies for this unsatisfactory behavior have been suggested. For instance, it has been proposed to raise the concentration and the temperature of the ammonia vapors, or to pass the incompletely developed print through the processing equipment a second time. It has also been proposed to enlarge the development chamber of automatic developing machines, thus permitting a longer contact with the ammonia vapors. However, all of these suggestions have either practical disadvantages or fail to give the desired results.

We have discovered that the foregoing shortcomings can be obviated by incorporating in the light sensitive layer a carboxamide characterized by the following general formulae:

$$RCONH_2$$

and

$$R_1NHCONH_2$$

wherein R is hydrogen, methyl, methoxy or ethoxy and R_1 is hydrogen, methyl or ethyl. This discovery makes it possible to process the diazo printing materials containing these carboxamides at higher rates of speed without loss of maximum density and permits complete coupling of the diazonium salts within a much shorter period of time than was heretofore possible. Moreover, the prints obtained are characterized not only by a greater density but also by a brighter appearance, thus improving the visual contrast., Furthermore, the finished prints are less subject to deterioration, dulling and discoloration since all of the diazonium salts remaining after the exposure to ultraviolet light have been combined with the couplers. Other advantages observed include the absence of any tendency to curl.

The amounts of carboxamide employed in the preparation of dry print paper, according to this invention, range from 100 to 500 grams per liter (ten to fifty percent) of a diazotype coating solution. Amounts ranging from 250 grams to 350 grams per liter of coating solution are preferred for practical reasons. Based on the total weight of non-volatile ingredients used in the preparation of the coating solution, the proportions vary from thirty to seventy per cent by weight of carboxamide, with forty five to sixty per cent representing the preferred percentage. The relationship with respect to the light sensitive diazo compound is such that the amount of carboxamide employed exceeds the amount of diazo compound by factors varying from three to one hundred fifty, factors between six and thirty-five being preferred.

The following are examples of carboxamides employed in accordance with the present invention:

$HCONH_2$

Formamide

CH_3CONH_2

Acetamide

H_2NCONH_2

Urea

$CH_3NHCONH_2$

Methylurea

$C_2H_5NHCONH_2$

Ethylurea

CH_3OCONH_2

Methylurethane (methyl ester of carbamic acid)

$C_2H_5OCONH_2$

Urethane (ethyl ester of carbamic acid)

In the coating solutions which are used for sensitizing the diazo paper according to this invention, any combination of diazo and coupling components which are suitable for the preparation of dry development (two component diazotype layers) and which will produce the shade desired for the final image may be employed.

Diazo compounds which are suitable for such two component diazotype layers are known to be those which are derived from 1,2- and 2,1-aminonaphthols, 1,4-aminonaphthols and aromatic p-diamines of the benzene series, particularly p-phenylenediamines which are mono- or di-substituted on one of the two amino groups. Examples of such diazo compounds which are commonly used in the production of diazotype images are the diazo derivatives of:

4-amino-N-methylaniline
4-amino-N-ethylaniline
4-amino-diphenylamine
4-amino-N-(β hydroxyethyl)aniline
4-amino-N-(2',6'-dibromobenzyl)aniline
4-amino-N,N-dimethylaniline
4-amino-N,N-diethylaniline
4-amino-N,N-dipropylaniline
4-amino-N-methyl-N-(β-hydroxyethyl)aniline
4-amino-N-(β-hydroxyethyl)aniline
4-amino-N-butyl-N-(β-hydroxyethyl)aniline
4-amino-N,N-di(β-hydroxyethyl)aniline
4-amino-N-benzyl-N-ethylaniline
4-amino-N-ethyl-3-methylaniline
4-amino-N,N-dimethyl-3-methylaniline
4-amino-N,N-dimethyl-2-methylaniline
4-amino-N,N-diethyl-3-methylaniline
4-amino-N-ethyl-N-(β-hydroxyethyl)3-methylaniline
4-amino-N-cyclohexyl-2-methoxyaniline
4-amino-N,N-di(β-hydroxyethyl)3-methoxyaniline
4-amino-N,N-diethylamino-3-ethoxyaniline
4-amino-3-chloro-N,N-di(β-hydroxyethyl)aniline
4-amino-3-carboxy-N,N-diethylaniline
1-amino-2-hydroxynaphthalene-4-sulfonic acid
2-amino-1-hydroxynaphthalene-5-sulfonic acid
2-amino-1-hydroxynaphthalene-3,6-disulfonic acid
3-aminocarbazol, and the like.

These diazo compounds are used in the form of their stabilized salts, as exemplified by p-diphenylamine diazonium sulfate or in the form of their zinc chloride or boron trifluoride double salts. As examples of such stabilized double salts, there may be mentioned the zinc chloride or boron trifluoride double salts of:

p-Diethylaminobenzenediazonium chloride
p - Di(β - hydroxyethyl)amino - 2 - methylbenzenediazonium chloride
p - Ethyl - (β - hydroxyethyl)aminobenzenediazonium chloride
p-Diethylamino-3-ethoxybenzenediazonium chloride, and the like.

The diazo compounds may also be used in the form of anhydride, as exemplified by:

2-amino-1-hydroxynaphthalene-4-sulfodiazonium anhydride
2 - amino - 1 - hydroxynaphthalene - 5 - sulfodiazonium anhydride
1 - amino - 2 - hydroxynaphthalene - 4 - sulfodiazonium anhydride
1 - amino - 2 - hydroxynaphthalene - 5 - sulfodiazonium anhydride and their water soluble alkali metal salts.

As examples of suitable azo coupling components, there may be mentioned:

Resorcinol
Phloroglucinol
3-hydroxyphenylurea
3-(N-3'-aminobenzoyl)aminophenol
3-(N-4'-aminobenzoyl)aminophenol
2,3-dihydroxynaphthalene
2,7-dihydroxynaphthalene
2,3-dihydroxynaphthalene-6-sulfonic acid
1-hydroxynaphthalene-4-sulfonic acid
2-hydroxynaphthalene-3,6-disulfonic acid
1-hydroxynaphthalene-3,8-disulfonic acid

2-amino-8-hydroxynaphthalene-3,6-disulfonic acid
2,3-dihydroxynaphthalene-6-carboxylic acid
1-amino-7-hydroxynaphthalene
1-amino-8-hydroxynaphthalene-3,6-disulfonic acid
4-hydroxybenzimidazole hydrochloride
2-hydroxy-7,8-naphthimidazole hydrochloride
8-hydroxy-1,2-naphthimidazole hydrochloride
7-hydroxy-1,2-naphthimidazole hydrochloride
2-hydroxynaphthalene-8-biguanide
7-hydroxynaphthalene-2-biguanide
7-hydroxynaphthalene-1-biguanide
8-hydroxynaphthalene-1-biguanide
2,2',4,4'-tetrahydroxydiphenyl
3,3',5,5'-tetrahydroxybiphenyl
4-hydroxyquinolone
1-methyl-4-hydroxyquinolone(2)
1-(2'-methoxyphenyl)-4-hydroxyquinolone(2)
1-phenyl-3-methylpyrazolone
1-(4'-sulfophenyl)-3-methylpyrazolone
1-tolyl-3-methylpyrazolone
Acetoacetanilide
Acetoacet-o-toluidide
Acetoacetic acid benzylamide, and the like.

Sulfonic or carboxylic acid substituted couplers may be used as such or in the form of their water soluble alkali metal salts. Variations in shade may be obtained by using more than one coupler. Similarly, blacks, which are uniformly neutral throughout the full density, and half-tone ranges can be prepared by the combined use of at least three selected coupling components in accordance with the procedure described in U. S. Patent 2,537,919.

Suitable carriers for diazo solutions not only include various types of paper such as ordinary wood pulp paper, rag type paper or document paper, but also textiles including fabrics made from cotton, batiste, regenerated cellulose of the xanthate or viscose type, balloon cloth, knitted rayon jersey, mixed cotton and rayon, or other absorbent, fibrous, woven or felted materials which can be impregnated with the diazo solutions.

The following specific examples are intended to be illustrative and are not to be considered as limiting the invention.

Example I

A wood pulp paper stock of medium weight was coated with a solution having the following composition:

Ethylene glycol	mls	5.0
Isopropanol	mls	1.0
Citric acid	gms	2.0
Thiourea	gms	5.0
2,3-dihydroxynaphthalene-6-sulfonic acid	gms	4.0
Zinc chloride double salt of p-diethylaminobenzenediazonium chloride	gms	0.9
Saponin	gms	0.1
Zinc chloride	gms	5.0
Acetamide	gms	30.0
Water to make	mls	100.0

The resulting sensitized paper was cut into sheets and exposed to ultra-violet light under a line pattern and developed with ammonia vapors in a commercial model of an ammonia developing machine operating at its maximum speed of 30 feet per minute. A brilliant blue print was obtained in which the blue areas had a density of 0.63. This density could not be increased by a repeated additional treatment with ammonia vapors.

Another paper coated with a coating solution identical with the one described above, with the exception that it did not contain any acetamide was exposed under the same line pattern and developed in the same machine under identical conditions. The density of the finished print was 0.49. This density could be increased to a value of 0.63 by subsequent treatment with ammonia vapors achieved by passing the print through the develop-

ing machine once more, while omitting a second light exposure. The two completely developed prints, namely, the one containing the acetamide and the other which had received a second development showed a good stability on aging and did not display any signs of discoloration or any other deterioration after being stored in daylight for several months. However, the print which did not contain the acetamide and had been incompletely developed, showed bad discoloration and deterioration at the end of this period.

Example II

A diazotype paper stock made of rag paper was coated with an aqueous solution having the following composition:

1-methyl-4-oxyquinolone-(2)	gms.	11.0
Zinc chloride double salt of p-diethylaminobenzenediazonium chloride	gms.	22.0
Ethyl alcohol	mls.	50.0
Citric acid	gms.	60.0
Thiourea	gms.	35.0
Zinc chloride	gms.	45.0
Formamide	gms.	400.0

Water to make 1 liter.

The resulting sensitized paper and a type paper prepared from a coating solution identical with the above, except that the formamide had been omitted were exposed under the same line pattern and developed in an ammonia developing machine operating at a speed of 24 feet per minute.

Although blue images were formed on both pictures, it was observed that the formamide-containing print had been developed to its maximum obtainable density of 0.62 and showed good keeping qualities, whereas the print prepared from the coating solution containing no formamide had a density of only 0.46 and was subject to dulling and fading during storage.

Example III

Example I was repeated with the exception that the 30.0 gms. of acetamide was replaced by 35.0 gms. of urea. The print containing the urea obtained its maximum achievable density of 0.64 when processed in the automatic developing machine running at a speed of 28 feet per minute whereas the type print which contained no urea had only a density of 0.48 corresponding to three-fourths of its maximum achievable density of 0.64.

Example IV

An aqueous solution of the following composition was prepared and applied to a starch-sized cotton cloth:

	Gms.
Zinc chloride double salt of 4-diethylamino-2-methylbenzenediazonium chloride	15.0
2,3-dihydroxynaphthalene	8.0
Citric acid	50.0
Zinc chloride	60.0
Urethane	220.0
Saponin	0.1

Water to make 1 liter.

After drying, the cloth was exposed and processed in an automatic ammonia developing machine operating at a speed of 24 feet per minute. The color obtained was a bright blue having excellent gradation characteristics and was superior in hue, density and keeping qualities to a picture obtained on a comparison coating which had been prepared in an analogous manner with the exception that urethane had been omitted.

Example V

An aqueous solution of the following formula was prepared and applied to a linen paper:

Isopropanol	gms.	10.0
Ethylene glycol	mls.	50.0

Citric acid	gms.	50.0
Thiourea	gms.	50.0
Saponin		0.1
Zinc chloride double salt of p-diethyl amino benzene diazonium chloride	gms.	50.0
2-hydroxy-7,8-naphthimidazole hydrochloride	gms.	20.0
Zinc chloride	gms.	35.0
Acetamide	gms.	300.0

Water to make 1 liter.

The resulting diazo paper was exposed to ultra-violet light under a line pattern, and subsequently developed with warm, moist ammonia vapors in a commercial model of an ammonia developing machine operating at a speed of 26 feet per minute. A maroon print was obtained which showed a higher dye density and had better keeping qualities than a comparison print which had been prepared from a coating solution identical to the one above, except that the acetamide had been omitted.

Example VI

A solution having the following composition was prepared and coated on a diazotype paper stock made of rag paper.

Resorcinol	gms.	25.0
Zinc chloride double salt of N-methyl-N-(β-hydroxyethyl)aminobenzenediazonium chloride	gms.	55.0
Citric acid	gms.	60.0
Thiourea	gms.	45.0
Isopropanol	mls.	15.0
Saponin	gms.	0.1
Zinc chloride	gms.	40.0
Ethylurea	gms.	350.0

Water to make 1 liter.

After drying, the paper was cut into sheets and exposed to ultraviolet light under a translucent sheet, having printed matter thereon, and developed with ammonia vapors in a diazotype printer. The sepia picture obtained showed greater dye density and had better keeping qualities than a comparison picture obtained on paper prepared from a coating solution identical with the one above, except that the ethylurea had been omitted.

Example VII

A coating solution having the following composition was coated on diazo stock paper:

Glycerin	mls.	50.0
Citric acid	gms.	50.0
Thiourea	gms.	50.0
Acetoacetanilide	gms.	0.8
2,3-Dihydroxynaphthalene	gms.	1.0
2,3-Dihydroxynaphthalene-6-sulfonic acid	gms.	40.0
Zinc chloride double salt of p-dimethyl aminobenzene diazonium chloride	gms.	25.0
Saponin	gms.	0.5
Zinc chloride	gms.	50.0
Acetamide	gms.	300.0

Water to make 1 liter.

The dried paper, cut into strips, was exposed under transparency and developed in a commercially available diazo printer operating at 25 feet per minute. A black reproduction of the transparency was obtained which was characterized by greater dye density, stability to aging and the absence of curl when compared with prints prepared from a coating solution identical with the one above, except that the acetamide had been omitted. The latter prints dulled and turned a brownish color within two months.

While there are disclosed above a number of embodiments of the invention herein described, it is obvious that various changes may be made without departing from the nature and spirit of the invention. Therefore, the inven-

tion is not limited to the specific details herein described except as defined in the appended claims.

We claim:

1. The process of producing a diazotype print which comprises applying to a suitable carrier a solution comprising a stabilized light-sensitive diazo compound, at least one coupling component and from ten per cent (10%) to fifty per cent (50%) by weight of a carboxamide selected from the class consisting of those corresponding to the following: $RCONH_2$ and $R_1NHCONH_2$ wherein R is a member selected from the class consisting of hydrogen, methyl, methoxy, and ethoxy and R_1 is a member selected from the class consisting of hydrogen, methyl and ethyl, drying said material, exposing the dried material with ultraviolet light through a pattern and developing the exposed material with ammonia vapors.

2. The process of producing a diazotype print which comprises applying to a suitable carrier a solution comprising a stabilized light-sensitive diazo compound, at least one coupling component and containing from ten per cent (10%) to fifty per cent (50%) by weight of urea, drying said material, exposing the dried material with ultraviolet light through a pattern and developing the exposed material with ammonia vapors.

3. The process of producing a diazotype print which comprises applying to a suitable carrier a solution comprising a stabilized light-sensitive diazo compound, at least one coupling component and containing from ten per cent (10%) to fifty per cent (50%) by weight of formamide, drying said material, exposing the dried material with ultraviolet light through a pattern and developing the exposed material with ammonia vapors.

4. The process of producing a diazotype print which comprises applying to a suitable carrier a solution comprising a stabilized light-sensitive diazo compound, at least one coupling component and containing from ten per cent (10%) to fifty per cent ((50%) by weight of acetamide, drying said material, exposing the dried material with ultraviolet light through a pattern and developing the exposed material with ammonia vapors.

5. The process of producing a positive diazotype print which comprises coating a paper base with a solution comprising a stabilized light-sensitive diazo compound, at least one coupling component and containing a carboxamide selected from the class consisting of those corresponding to the following formulae: $RCONH_2$ and

$R_1NHCONH_2$

wherein R is a member selected from the class consisting of hydrogen, methyl, methoxy and ethoxy, and R_1 is a member selected from the class consisting of hydrogen, methyl and ethyl, said solution containing more than ten per cent (10%) and less than fifty per cent (50%) by weight of said carboxamide, drying said coated paper, exposing said paper with ultraviolet light through a pattern and developing the exposed paper with ammonia vapors.

6. The process of producing a positive diazotype print which comprises coating a paper base with a solution comprising a stabilized, light-sensitive diazo compound, a coupling component and containing more than ten per cent (10%) and less than fifty (50%) of urea, drying the coated paper, exposing said paper with ultraviolet light through a pattern and developing the exposed paper with ammonia vapors.

7. The process of producing a positive diazotype print which comprises coating a paper base with a solution comprising a stabilized, light-sensitive diazo compound, a coupling component and containing more than ten per cent (10%) and less than fifty per cent (50%) of formamide, drying the coated paper, exposing said paper with ultraviolet light through a pattern and developing the exposed paper with ammonia vapors.

8. The process of producing a positive diazotype print which comprises coating a paper base with a solution comprising a stabilized, light-sensitive diazo compound, a coupling component and containing more than ten per cent and less than fifty per cent (50%) of acetamide, drying the coated paper, exposing said paper with ultraviolet light through a pattern and developing the exposed paper with ammonia vapors.

9. A diazotype light-sensitive material comprising on a suitable base a stabilized light-sensitive diazo compound and a coupling component, together with a carboxamide selected from the class consisting of those corresponding to the following formulae: $RCONH_2$ and $R_1NHCONH_2$ wherein R is a member of the class consisting of hydrogen, methyl, methoxy and ethoxy and R_1 is a member of the class consisting of methyl and ethyl, the carboxamide being present in such proportions that its weight exceeds by a factor of not less than three and not more than one hundred fifty the weight of the diazo compound.

10. A diazotype light-sensitive material comprising on a suitable base a light-sensitive diazo compound and a coupling component together with formamide, the amount of the latter exceeding by a factor of not less than three and not more than one hundred fifty the weight of diazo compound present.

11. A diazotype light-sensitive material comprising on a suitable base a light-sensitive diazo compound and a coupling component together with acetamide, the amount of the latter exceeding by a factor of not less than three and not more than one hundred fifty the weight of diazo compound present.

12. A light-sensitive diazotype photoprinting material comprising a paper support coated with a sensitizing solution containing a stabilized light-sensitive diazo compound and an azo coupling component together with a carboxamide selected from the class consisting of those corresponding to the following general formulae:

$RCONH_2$

and $R_1NHCONH_2$ wherein R is a member selected from the class consisting of hydrogen, methyl, methoxy and ethoxy, and R_1 is a member selected from the class consisting of methyl, and ethyl, the quantity of said carboxamide being not less than thirty per cent (30%) and not more than seventy per cent (70%) by weight of the total non-volatile ingredients of said sensitizing solution.

13. A light-sensitive diazotype photoprinting material comprising a paper support coated with a sensitizing solution comprising a stabilized light-sensitive diazo compound and an azo coupling component and containing formamide in such quantity that it represents not less than thirty per cent (30%) and not more than seventy per cent (70%) of the total non-volatile ingredients of said sensitizing solution.

14. A light-sensitive diazotype photoprinting material comprising a paper support coated with a sensitizing solution comprising a stabilized light-sensitive diazo compound and an azo coupling component and containing acetamide in such quantity that it represents not less than thirty per cent (30%) and not more than seventy per cent (70%) of the total non-volatile ingredients of said sensitizing solution.

15. A diazotype light-sensitive material comprising on a suitable base, a uniform coating of a stabilized light-sensitive diazo compound and a coupling component, together with a carboxamide selected from the class consisting of those corresponding to the following formulae: $RCONH_2$ and $R_1NHCONH_2$ wherein R is a member of the class consisting of hydrogen, methyl, methoxy and ethoxy and R_1 is a member of the class consisting of methyl and ethyl, the carboxamide being present in such proportions that its weight exceeds, by a factor of not less than six and not more than thirty-five, the weight of the diazo compound.

16. A diazotype light-sensitive material comprising on a suitable base, a uniform coating of a light-sensitive diazo compound and a coupling component together with

formamide, the amount of the latter exceeding, by a factor of not less than six and not more than thirty-five, the weight of diazo compound present.

17. A diazotype light-sensitive material comprising on a suitable base, a uniform coating of a light-sensitive diazo compound and a coupling component together with acetamide, the amount of the latter exceeding, by a factor of not less than six and not more than thirty-five, the weight of diazo compound present.

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