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PROCESS OF APPLYING A DIAZOTYPE PHOTOPRINTING
MATERIAL TO A BASE AND THE RESULTANT ARTICLE
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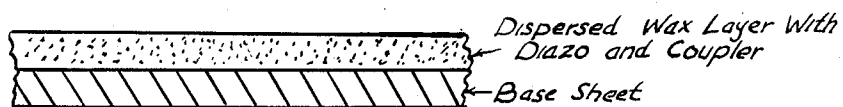


Fig. I.

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2,807,545

PROCESS OF APPLYING A DIAZOTYPE PHOTO-PRINTING MATERIAL TO A BASE AND THE RESULTANT ARTICLE

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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. Since the dyestuff components, as coated on the carrier, are relatively unstable and since they tend to couple prior to alkaline development, the coating solution also usually contains small amounts of an acid such as citric acid, tartaric acid, tricarballic 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 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, 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.

In the foregoing diazotype process or system, in sufficient fastness of the colored image to washing presents a serious problem. Thus, limits are imposed on the choice of components available for image formation. Often the selection of desired colors or color combinations is precluded, particularly when the finished prints are to be contacted with water or even when stored under conditions of high humidity. Moreover, such lack of wash fastness manifests itself in most diazotype photoprinting materials by the darkening of the background areas arising from discoloration of residual image-forming components, decomposition or bleaching of the images formed.

Other disadvantages often encountered in the manufacture of diazotype photoprinting materials are the tendency of the sensitized layers to decompose or couple prematurely under humid storage conditions.

A great variety of remedies have been proposed to overcome these objections. Many of these involve treatments which, while improving one of the desired properties of the photoprinting materials, have an undesired effect on other properties. For instance, methods which serve to improve the fastness to washing may cause an undesirable increase in background discoloration or re-

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duce the photosensitivity of the material, cause loss of storage stability before exposure, decrease the rate of development or interfere with the storage stability of the finished print.

It is an object of this invention to overcome the disadvantages previously described. These and other objects and advantages of this invention will hereinafter appear and for purposes of illustration, but not of limitation, an embodiment of the invention is shown in the accompanying drawing in which—

Figure 1 is a schematic sectional elevational view through a structure embodying the features of this invention.

I have found that the foregoing shortcomings can be obviated by adding to the diazotype coating solution, a wax or wax-like material in the form of a dispersion which is sufficiently stabilized to remain in the dispersed state even in the presence of the electrolytes used in the sensitized solution. This discovery makes it possible to obtain diazotype materials which display greatly improved wash fastness without the manifestation of any of the previously mentioned deleterious side effects. For example, the water resistance of the print is increased to such an extent that the materials can be stored out of doors under conditions which would destroy ordinary diazotype prints.

The amounts of wax dispersions employed in the preparation of dry print paper according to this invention, range from 3 grams to 70 grams of solid wax per liter of a diazotype coating solution. In other words, the quantity of wax by weight based on the total weight of non-volatile ingredients used in the preparation of the coating solution should be from 1 to 28%.

The wax compositions utilized in accordance with my invention are prepared by dispersing in water, a wax having a melting point higher than 110° F. (43.3° C.) with the aid of a surface active agent. Suitable waxes include beeswax, carnauba wax, cerosin wax, Chinese wax, flax wax, godang wax, Java wax, insect wax, paraffin wax, montan wax and ceresin wax, spermaceti wax, stearic acid and the like. Among the chemically identified compounds present in these waxes are esters derived from long chain monohydric alcohols and long chain esters, high molecular weight hydrocarbons, fatty acids, alcohols and ketones.

The aforesaid waxes may be amorphous or microcrystalline and can be used alone or in the form of mixtures. It is important, however, to select waxes which are colorless or only slightly colored in order to avoid any background discoloration of the diazotype print.

The waxes are dispersed by the use of suitable surface active agents of the cationic, anionic or non-ionic type. A great number of these agents have been described in the literature and the following which I have found suitable are illustrative:

The reaction products of long chained aliphatic amines such as laurylamine and stearylamine with ethylene oxide;

The esters of long chained fatty acids with tertiary amino alcohols, i. e., stearyl triethanolamine and oleyl triethanolamine;

The reaction products of ethylene oxide and propylene oxide with a phenol or an alcohol, e. g., the reaction products of from 8 to 20 moles of ethylene oxide with dodecylphenol or oleyl alcohol;

The esters of long chained fatty acids such as stearic or lauric and anhydrosorbitol as well as their reaction products with ethylene oxide;

Glycol esters such as those obtained by reacting oleic acid with at least 6 molar equivalents of ethylene oxide;

Long chained fatty acid esters of pentaerythritol and dipentaerythritol, i. e., such esters of stearic and lauric acid;

Ethers obtained by the etherification of long chained alcohols and glycols, e. g., the reaction products of oleyl alcohol and di- or tri-ethylene glycol, glycerol or polyglycerol;

The reaction products of fatty acid ethanol amides and formaldehyde;

Ammonium or alkali metal sulfonates of carboxylic acid amides, e. g., sodium cetyl propionamide- β -sulfonate or sodium naphthenylacetamide trisulfonate;

Sodium lauryl sulfate, sodium dioctyl sulfosuccinate;

Water soluble polymeric carboxylic acids, e. g., the polymers or mixed polymers of acrylic, methacrylic and maleic acid;

The mono-, di-, tri-ethanolamine, diethylamine, triethylamine or morpholine salts of long chained fatty acids such as palmitic, stearic or oleic acid.

In lieu of using a separate dispersing agent, it is possible where the wax contains a long chained fatty acid to effect dispersion by the addition of a base such as an alkylolamine, morpholine, diethylamine and the like. In this case, the base reacts with the acid and forms a dispersing agent in situ.

It is advisable to use dispersions in which the wax particles have a size ranging from 0.1 to 5 microns. Waxes meeting this requirement are available on the open market. The particle size of any wax dispersion selected for use, moreover, can be readily ascertained by observation under the microscope.

The addition of small amounts of polyvinyl alcohol or similar colloidal carriers is occasionally useful for the purpose of further stabilizing the dispersion after the latter is added to the coating solution.

In order to avoid any undesirable excessive dilution of the diazo coating solution, the wax dispersions are diluted with a portion of the water which is used to adjust the coating solution to its final volume.

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 paper (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 disubstituted 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-aminocarbazole and the like.

These diazo compounds are used preferably 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 anhydrides, 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'-tetrahydroxydiphenyl
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

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with the procedure described in United States Patent 2,537,919.

Suitable carriers for diazo solutions include not only various types of paper such as ordinary wood pulp paper, rag type paper or document paper, and photographic film base such as cellulose acetate, cellulose acetate butyrate and the like, but also textiles including fabrics made from cotton, cellulose acetate, 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. Frequently, carriers used in the manufacture of diazotype materials are surface coated with an aqueous dispersion containing a resinous binder and a white pigment such as silica, barium sulfate, zinc oxide, titanium dioxide, clay, talcum and the like.

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

Example I

A dispersion was prepared by heating and agitating the following composition:

	Percent
Paraffin wax (white).....	40.0
Sorbitan monopalmitate.....	3.5
Ethylene oxide reaction product of sorbitan monopalmitate.....	3.5
Polyvinyl alcohol.....	1.0
Water to make.....	52.0

Five milliliters of this wax emulsion were diluted with 15 milliliters of water and added with stirring to the following diazotype coating solution:

Ethylene glycol.....	cc..	5.0
Isopropanol.....	gms..	2.0
Citric acid.....	gms..	5.0
Thiourea.....	gms..	4.0
Zinc chloride.....	gms..	5.0
2,3-dihydroxynaphthalene-6-sulfonic acid.....	gms..	3.0
Zinc chloride double salt of p-diethylaminobenzene diazonium chloride.....	gms..	2.0
Saponin.....	gm..	0.1
Water to make.....	mls..	80.0

The coating solution thus obtained was coated on pigment precoated paper stock of medium weight and dried. The resulting sensitized paper was cut into sheets and exposed to ultraviolet light under a density step wedge and developed with ammonia in a commercial model of an ammonia developing machine. A comparison sample prepared with a coating solution identical with the one described above with the exception that it did not contain any dispersed wax was exposed under the same density wedge and developed on the same machine.

A comparison of the two prints showed that the one prepared from the coating solution containing the wax dispersion was far superior to the other with respect to fastness to washing as evidenced by the behaviour of the prints when wetted with water, or when stored out of doors exposed to rigid weather conditions. In addition, the print containing the wax had a whiter background and displayed a greater brightness. The feathering of ink lines which is commonly apparent when writing with ink on diazotype prints was also remarkably reduced. Improvements were also noted in the shearing, folding and plying characteristics. The tendency of the material to stick when moving through the developing machine, to curl and to crock was greatly reduced.

Example II

Six milliliters of a dispersion containing 40 parts of microcrystalline paraffin wax, 1 part each of triethanolamine and polyvinyl alcohol and .1 part of zirconium stearate were diluted with 20 milliliters of water and

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added to a coating solution having the following composition:

Resorcinol.....	gms..	2.5
Zinc chloride double salt of p-N-methyl-N-(β -hydroxyethyl)aminobenzene diazonium chloride.....	gms..	4.5
Citric acid.....	gms..	6.0
Thiourea.....	gms..	4.0
Isopropanol.....	mls..	1.5
Saponin.....	gm..	.01
Zinc chloride.....	gms..	5.5
Water to make.....	mls..	75.0

The resulting solution was coated onto a diazotype paper stock. After drying, the diazo paper was cut into sheets which were exposed to ultraviolet light under a line pattern and developed with ammonia vapors in a commercial ammonia developing machine. The print was superior to that obtained while omitting the wax to the same extent as that obtained in Example I.

Example III

Twenty five grams of beeswax were melted and dispersed in 200 milliliters of water by means of 3 grams of oleic acid, 2.25 grams of aminopropanol and .5 gram of borax dissolved in 15 grams of water. Ten milliliters of the resulting dispersion were added to a diazo coating solution having the following composition:

Glycerin.....	mls..	5.0
Citric acid.....	mls..	5.0
Thiourea.....	gms..	5.0
Acetoacetanilide.....	gm..	0.08
Resorcinol.....	gm..	.3
2,3-dihydroxynaphthalene-6-sulfonic acid.....	gms..	2.0
Zinc chloride double salt of p-dimethylaminobenzene diazonium chloride.....	gms..	2.5
Saponin.....	gm..	0.05
Zinc chloride.....	gms..	4.5
Water to make.....	mls..	90.0

The resulting diazo coating solution was coated on linen paper which was dried, cut into sheets, exposed to ultraviolet light under a transparency, and developed in a commercial ammonia developing apparatus. A black reproduction of the transparency was obtained which was characterized by far superior properties than a print which had been prepared from a coating solution from which the wax dispersion had been omitted.

Example IV

An aqueous wax composition was prepared by dispersing a melt of 30 parts of bleach carnauba, 12 parts of white beeswax and 28 parts of paraffin wax in a solution containing 10 parts of polyoxyalkylene sorbitan mono-laureate and 5 parts of morpholine in 200 parts of water at a temperature of 180° F. Fifty milliliters of the resulting dispersion were added to a diazo coating solution having the following composition:

Isopropanol.....	gms..	10.0
Ethylene glycol.....	mls..	50.0
Citric acid.....	gms..	50.0
Thiourea.....	gms..	50.0
Saponin.....	gm..	.1
Zinc chloride double salt of p-diethylaminobenzene diazonium chloride.....	gms..	20.0
2-hydroxy-7,8-naphthimidazole hydrochloride.....	gms..	24.0
Zinc chloride.....	gms..	50.0
Water to make.....	mls..	950.0

The resulting solution was coated on a diazotype paper stock made of rag paper which was allowed to dry and then exposed under a printed pattern and developed in an atmosphere of ammonia. A maroon print was obtained which showed much better properties than a com-

parison print which had been prepared from a coating solution which was identical excepting that it did not contain any wax.

Example V

Example I was repeated with the exception that the paraffin wax was replaced by an equal weight of spermaceti wax. The results obtained were identical with those described in Example I.

It has been stated above that the prints obtained herein do not show any tendency toward feathering when written upon with ink. It is well known that paper impregnated with wax, i. e., the so-called waxed papers, cannot take an ink impression from a pen. This is due to the fact that the wax causes a general smearing of each character impressed thereon. Since my prints carry wax on the surface or embedded therein, it was to be expected that any attempt to write thereon with ink would either cause excessive smearing or marked feathering. The fact that neither result ensues, but that clear, well defined characters are obtained is, therefore, surprising to say the least.

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

I claim:

1. A diazotype photoprinting material having a base carrying a single light sensitive layer comprising a light sensitive diazonium compound, a coupling component, a finely divided wax and a surface active dispersing agent capable of dispersing said wax in water, the amount of wax ranging from about 1 to 28% by weight of the total solids of said sensitive layer.
2. A diazotype light sensitive material according to claim 1 wherein said wax is paraffin wax.
3. A diazotype light sensitive material according to claim 1 wherein said wax is carnauba wax.
4. A diazotype light sensitive material according to claim 1 wherein said wax is spermaceti.
5. A diazotype light sensitive material according to claim 1 wherein said wax is beeswax.
6. The process of producing a diazotype photoprinting material which comprises applying to a base, an aqueous solution comprising a light sensitive diazo compound, a coupling component and a dispersion of wax in an aqueous medium dispersed by the use of a surface active dispersing agent, said wax being present in amounts ranging from 3 grams to 70 grams per liter of coating solution.
7. The process of producing diazotype photoprinting material according to claim 6 wherein said wax is paraffin wax.
8. The process of producing a diazotype photoprinting material according to claim 6 wherein said wax is carnauba wax.

9. The process of producing a diazotype photoprinting material according to claim 6 wherein said wax is spermaceti.

10. The process of producing diazotype photoprinting material according to claim 6 wherein said wax is beeswax.

11. A diazotype photoprinting material having a base carrying a single light sensitive layer comprising a light sensitive diazonium compound, a coupling component, a finely divided wax and a surface active dispersing agent capable of dispersing said wax in water, the amount of wax ranging from about 1 to 28% by weight of the total solids of said sensitive layer, said wax having a particle size ranging from 0.1 to 5 microns and melting above 110° F.

12. A coated base comprising a paper sheet and a continuous coating on said sheet, said coating comprising a wax in finely divided form as a base containing a soluble phenolic diazo dye coupler and a soluble salt of a diazo dye intermediate free of color, said salt and coupler being capable of reacting under alkaline conditions to form an azo dyestuff, said salt of a diazo dye intermediate being p-diethylaminobenzene diazonium chloride.

13. A coated base comprising a paper sheet and a continuous coating on said sheet, said coating comprising a wax in finely divided form as a base containing a soluble phenolic diazo dye coupler and a soluble salt of a diazo dye intermediate free of color, said salt and coupler being capable of reacting under alkaline conditions to form an azo dyestuff, said salt of a diazo dye intermediate being p-dimethylamino benzene diazonium chloride.

14. A coated base comprising a paper sheet and a continuous coating on said sheet, said coating comprising a wax in finely divided form as a base containing a soluble phenolic diazo dye coupler and a soluble salt of a diazo dye intermediate free of color, said salt and coupler being capable of reacting under alkaline conditions to form an azo dyestuff, said salt of a diazo dye intermediate being p-ethylhydroxyethylaminobenzene diazonium chloride.

15. A coated base comprising a paper sheet and a continuous coating on said sheet, said coating comprising a wax in finely divided form as a base containing a soluble phenolic diazo dye coupler and a soluble salt of a diazo dye intermediate free of color, said salt and coupler being capable of reacting under alkaline conditions to form an azo dyestuff, said salt of a diazo dye intermediate being p-diphenylaminobenzene diazonium chloride.

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