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TWO-COMPONENT HEAT DEVELOPING DIAZOTYPES

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ABSTRACT OF THE DISCLOSURE

A heat-developable, two-component diazotype photoprinting material which comprised a support and a light-sensitive layer containing an azo coupling component, a light-sensitive diazonium compound, a neutral to acid reagent yielding an alkaline reacting compound on heating to a temperature of 100–200° C. and retrograded starch was prepared.

This invention relates to two-component diazotype photoprinting material susceptible to development on heating, wherein said light-sensitive two-component diazotype layer comprises a neutral to acid reacting reagent yielding an alkaline reacting compound on heating and a starch binder.

Two-component diazotype photoprinting material comprises a supporting sheet, such as paper or film, having in a surface coating or layer, an azo coupling component and a light-sensitive diazonium compound stabilized against premature coupling by inclusion of an acid stabilizer. On exposure of such coating to actinic light under an opaque pattern on a translucent background, the light-sensitive diazonium compound is destroyed in the light-struck areas and on subsequent exposure to an alkaline development medium, such as gaseous ammonia, the acid stabilizer is neutralized and the residual diazonium compound couples with the coupling component to form an azo dye image in the areas corresponding to the opaque portions of the original pattern. Photoprinting materials of this type have met with various objections, such as the inconvenience associated with alkaline development and the need for special equipment to avoid obnoxious ammonia odors.

It has been proposed to include in a two-component light-sensitive diazotype layer of the aforesaid nature, one or more reagents having an acid to neutral reaction which, on heating, are converted or decomposed to yield an alkaline reacting compound. Diazotype photoprinting materials containing such reagents can be developed after exposure to light under a pattern as mentioned above by heating at a temperature causing the aforesaid modification or decomposition. The alkaline reaction product thereby formed neutralizes the acid stabilizer and causes image-wise coupling of the residual diazonium compound with the azo coupling component. Premature coupling of the diazonium compound during storage has tended to destroy the desired contrast in many cases.

Numerous attempts have been made in the prior art to obviate some of these problems. Thus, it has been proposed to prepare and apply the individual diazonium salts and coupling materials to photographic sheets in such a manner that they will form azo dyes under heat alone. An example is contained in U.S. Patent 2,418,623. This patent proposed to use a biguanidine salt and a diazo compound which would decompose under the influence of heat to yield ammonia as a developing agent.

A number of other prior art investigators have suggested that the diazonium salts and couplers might be developed by heat, provided they are applied in separate

layers or coatings, the application of the separate coatings to be such as to avoid premature reaction between them. U.S. Patent 3,046,128 discloses a typical heat developing two-component diazotype of this type wherein a light-sensitive diazonium layer is applied to one side of a fairly porous sheet of paper and an alkali generating layer is applied to the opposite side of the paper. The alkali generating layer contains materials having a vapor pressure such that at room temperature or slightly above room temperature the alkaline material has a low vapor pressure and at temperatures of about 200 to 400° F. the alkali material has substantial vapor pressure. The alkaline material either breaks down and passes as a vapor through the paper or merely passes through the paper without any chemical breakdown. Various materials such as urea, guanidine, alkyl substituted ureas, ammonia salts of weak acid, volatile organic basic materials (ethylenediamine) are suggested. While this method has certain advantages it is relatively difficult to package more than one sheet of this material together without a reasonable chance of premature development of the diazotype layer. Figure 3 of this patent discloses the use of a vapor barrier film as a top coat for the diazo layer. This layer can obviate the aforesaid disadvantages. However this increases the cost of the final product unduly. Systems of this type also have the disadvantage that the coupling rate of the diazotype components is relatively slow because of the slow rate at which the alkaline material reaches the reaction zone.

It has also been suggested in some instances that the alkaline material be physically separated in some manner and only brought together later for development purposes. U.S. Patent 3,076,707 illustrates one method of accomplishing this. The patentees disclose forming a nonreactive crystalline complex of a basic material such as an amine, and a phenolic compound or urea. This crystalline complex is decomposed after exposure of the diazotype material by the influence of heat.

The use of alkaline generating agents, such as urea or trichloroacetic acid (sodium trichloroacetate in an acidic system) for coupling has also been proposed in the prior art. A reaction would take place subsequently on heating. However, urea decomposes below moderate storage temperature and even at normal room temperature. Furthermore, relatively large amounts of urea are required for satisfactory development. Note for example U.S. Patent 3,046,128 which suggests using up to 3,000 grams of urea per one thousand square feet of diazotype paper. It is difficult to store materials of this type and maintain proper quantities over moderate periods of time. Sodium trichloroacetate also tends to cause the diazonium salt to decompose prematurely thereby reducing dye density and brightness of image areas.

Each of these schemes however involves certain practical difficulties and none of them has been widely successful. Heating diazotype paper to 100 to 200° C. cannot be carried out without causing some degradation of the diazo compound. Density and brightness of the image obtained is accordingly dependent upon the coupling speed of the diazonium compound, the speed with which the alkaline material is made available to promote the coupling reaction and the rate at which the diazonium compound is decomposed. It is accordingly desirable to use fast coupling diazotype components and readily available sources of alkali. However the faster the coupling speed of the components, the poorer the shelf life of the diazotype. Correspondingly, the more readily available the alkaline source the more danger of premature coupling. Further, the neutral to acid salts of trichloracetic acid, which are particularly advantageous readily available sources of

alkali on heating, tend to cause premature decomposition of diazonium salts.

It has been proposed to improve the brightness and dye density of two-component diazotype materials by using silica and/or alumina in the sensitizing composition and/or in a precoating. However there have been various problems connected with this use since the pigmented material has a tendency to be removed from the surface of the paper under normal handling conditions. In order to remedy these drawbacks, various combination of materials have been suggested as suitable binders.

The object of this invention is to provide heat developing two-component diazotype materials having improved dye density and brightness. Another object of this invention is to provide heat developing two-component diazotypes wherein the improved dye density and brightness is the direct result of an additive having no deleterious effect on the shelf stability of two-component diazotype materials. A further object of this invention is to provide heat developing two-component diazotype materials having these properties to a high degree wherein an alkaline source comprising a neutral to acid salt of trichloroacetic acid is contained in the two-component diazotype layer.

We have now found that the objects of our invention can be accomplished by providing a heat developing two-component diazotype containing a starch binder. This invention utilizes the changes in physical properties of the starch material. Unlike many uses of starch in diazotype photoprinting materials where the starch is used in the granular form for its light defraction properties, etc., the starch in our invention must be used in the pasted form. On pasting in water the granular starch changes from a relatively inert water-insoluble material, which can be readily isolated by filtration from the mother liquor, into a colloidal dispersion, which cannot be separated from the mother liquor by filtration. During the pasting operation (heating in water at about 70–90° C. or higher) the hydrogen bonding between the various starch molecules is destroyed and a colloidal starch dispersion is formed. The starch paste, which contains the diazotype sensitizing composition of this invention, is then applied to a suitable substrate. As the sensitizing composition dries, the colloidal starch retrogrades forming a water-insoluble layer, which tenaciously bonds the components of the heat-sensitive two-component diazotype together and to the substrate. During retrogradation and drying the hydrogen bonding of the starch molecules is reestablished. The retrograded starch is more resistant to subsequent dispersion in water than the starting granular starch.

This bonding characteristic of the starch makes it possible to use materials such as silica and/or alumina to the best advantage. The insoluble starch reduces markedly the tendency of silica and/or alumina to powder off from the surface of the diazotype layer. Further, the starch dries to a white material which aids in emphasizing the contrast between the colored image areas and the white background areas. The retrograded starch also tends to insulate the light sensitive diazonium compound from materials, such as sodium trichloroacetate, which reacts deleteriously with the diazonium compound. Accordingly, dye density and brightness is improved.

For the purpose of this invention the term "starch" refers to native starches such as corn starch, high amylose corn starch, waxy maize, potato starch, rich starch, wheat starch, tapioca starch and the fractions thereof (amylose and/or amylopectin) which are capable of forming a starch dispersion. The starch can be unmodified, modified or derivatized. In general all the unmodified native starches and modified starches (alkaline hypochlorite oxidized, acid modified and dextrinized starches) are capable of forming a starch dispersion.

The water-dispersibility of starch derivatives is dependent on the degree of substitution (D.S.) of the starch derivative, the functionality of the derivatizing agent and whether the derivatizing agent has any solubilizing groups. For example, starch derivatives formed by reacting starch with etherifying agents such as ethylene oxide, propylene oxide, N,N-diethylaminoethyl chloride, chloroacetic acid, etc. are water-dispersible at essentially all degrees of substitution. Starch ethers formed by reacting starch with etherifying agents such as acrylonitrile and styrene oxide are water-dispersible at low D.S. but insoluble at high D.S. The water-dispersibility of starch esters varies in the same manner as the ethers. Starch esters formed by reacting starch with cyclic anhydrides (maleic anhydride and succinic anhydride) under non-forcing conditions result in half-esters of starch which are dispersible at essentially all degrees of substitution. Starch esters formed by reacting starch with esterifying reagents such as acetic anhydride, vinyl acetate, propionic anhydride, stearic anhydride, etc. are water-dispersible at low degrees of substitution. Normally as the chain length of esterifying agent increases, the maximum D.S. at which the starch ester is water-dispersible decreases.

From an economic point of view it is rarely desirable to use a starch derivative having a D.S. above about 0.15. Almost all commercially available starches are of this order of degree of substitution. Generally the modified starches and derivatized starches are employed in order to obtain a starch dispersion having the desired viscosity at the desired total solids and set back properties. Accordingly, one or more of the above modifications or derivatizations can be employed in order to attain the desired properties. Generally the starch comprises from about 0.5 to 25 parts by weight per part by weight diazonium compound.

If desired the starch can be derivatized with a polyfunctional reagent such as phosphorus oxychloride, acrolein, epichlorohydrin or the like. However, extreme care must be taken in order to form a pastable product.

In some cases pasting of the starch may be carried out at room temperature using commercially available prepasted (pregelatinized) or cold-water-soluble starches.

Heat responsive reagents having an acid to neutral reaction at room temperature, which are adapted to yield on heating to temperatures of 100 to 200° C. an alkaline reacting compound for neutralizing the acid in a light-sensitive photoprinting material of this invention, include alkali metal salts of strong organic acids which are decomposed on heating to form basic compounds such as alkali metal salts of malonic, oxalic, maleic or benzene sulphinic acids; alkali metal salts of aliphatic monocarboxy acids of 1 to 3 carbon atoms having negative chain substituents such as halogen, CN or NO_2 in alpha or beta positions; and of these, especially the alkali metal (e.g. Na, K), ammonium and nitrogen base salts of trichloroacetic acid.

The sensitizing compositions of this invention may contain as light-sensitive stable diazonium compounds, those listed in U.S. Patent 2,501,874 and in the article by Van der Grinten in Photographic Journal volume 92(B), page 46. They are especially diazonium compounds derived from N-mono or N-di-substituted p-phenylenediamines, e.g., diazotization products of:

N,N-dimethyl-p-phenylenediamine
N,N-diethyl-p-phenylenediamine
N-benzyl-N-ethyl-p-phenylenediamine
N-ethyl-para-phenylenediamine
N,N-diethyl-2-ethoxy-p-phenylenediamine
N,N-bis-hydroxyethyl-p-phenylenediamine
N-ethyl-2-methyl-p-phenylenediamine
N-beta-hydroxyethyl-N-methyl-p-phenylenediamine
4-morpholinophenylamine

These compounds are preferably stabilized in the form of their double salts with zinc chloride, tin chloride, cadmimum chloride and the like.

Azo coupling components which can be incorporated in the materials of the invention are for example

2-(m-hydroxyphenoxy)ethanol
2,3-dihydroxynaphthalene
1,8-dihydroxynaphthalene
Phloroglucinol
Resorcinol
Octylresorcinol
Alpha-resorcylamid
3-methyl-1-phenyl-5-pyrazolone
Acetoacetanilide
H-acid
2,3-dihydroxynaphthalene-6-sulfonic acid
2,5-xylenol
2-methyl resorcinol

Acid stabilizers such as citric acid, tartaric acid, boric acid, acetic acid and similar acid reacting compounds are used to prevent premature coupling of the diazonium salt and azo coupling component.

In addition to the foregoing materials there can also be included reagents commonly employed in diazotype photoprinting materials, as for example, intensifiers such as ammonium sulfate, zinc chloride or nickel sulfate; stabilizing agents such as thiourea, or thiosinamine; accelerators such as 1-allyl-3-beta-hydroxy-ethyl-thiourea or 1-allyl-thioura; hygroscopic agents such as glycol or glycerin; and wetting agents such as saponin, lauryl sulfate, keryl benzene sulfonate or oleyl-N-methyltaurine.

The components of the sensitizing composition are preferably incorporated in a single solution or suspension and applied in a single coating step to the base. The latter may be paper, or film such as regenerated cellulose, cellulose acetate or other plastic films. However, the various components of the sensitizing composition can be applied, if desired, in successive coatings—one containing, for example, the diazonium salt, and another the alkali generating heat-sensitive reagent, the azo coupling component being incorporated in either of the two layers.

The material coated in accordance with the invention is developed after exposure under an opaque pattern on a translucent background, by heating at tempratures between 100 and 200° C., and preferably between 120–180° C., at which decomposition or conversion of the acid to neutral reagent to an alkaline reacting compound occurs. This promotes coupling of the residual diazonium compound with the azo coupling component.

The following examples are merely illustrative and should not be construed as limiting the scope of this invention. In the examples that follow, parts and percentages are by weight unless otherwise indicated.

Example 1

A paper base was sensitized with the following heat developing formulation:

	Parts by weight
Citric acid	0.5
Sodium 6,7-dihydroxynaphthalene-2-sulfonate	2
Sodium 1,3,6-niphthalene trisulfonate	1
Magnesium chloride	1
Acetamide	5
Sodium trichloroacetate	4
Starch acetate (D.S. 0.05)	4
4 - N,N - dimethylaminobenzenediazonium chlorozincate	0.5
Silica	4
Polyvinyl acetate emulsion	5
Water	100

The sensitizing composition was prepared in the normal manner except that the starch was pasted in water at 90° C. in about 20 parts by weight water. The base was dried and exposed to light under a translucent original containing opaque image areas. The exposed paper was developed by passing it through a heated chamber having temperatures of 120°–150° C. A blue dye of good density and brigthness was formed in the image areas of the heat developed print. The dye density was better than was obtained without the use of the starch acetate in the sensitizing solution.

Example 2

A paper base was sensitized with the following heat developing formulation:

	Parts by weight
Citric acid	0.5
Sodium 6,7-dihydroxynaphthalene-2-sulfonate	2
Sodium 1,3,6-naphthalene trisulfonate	1
Magnesium chloride	1
Acetamide	5
Sodium trichloroacetate	4
N,N-diethylaminoethyl starch (D.S. 0.02)	4
4 - N,N - dimethylaminobenzenediazonium chlorozincate	0.5
Silica	4
Polyvinyl acetate emulsion	5
Water	100

The sensitizing composition was prepared in the normal manner except that the starch was pasted in water at 90° C. in about 20 parts by weight water. The base was dried and exposed to light under a translucent original containing opaque image areas. The exposed paper was developed by passing it through a heated chamber having temperatures of 120–150° C. A blue dye of good density and brightness was formed in the image areas of the heat developed print. The dye density was better than was obtained without the use of the starch ether in the sensitizing solution. Essentially the same results can be obtained using unmodified corn starch, hypochlorite oxidized starch and acid modified starch.

Example 3

A paper base was sensitized with the following heat developing formulation:

	Parts by weight
Citric acid	0.5
Sodium 6,7-dihydroxynaphthalene-2-sulfonate	2
Sodium 1,3,6-naphthalene trisulfonate	1
Magnesium chloride	1
Acetamide	5
Sodium trichloroacetate	4
Dextrin	4
4 - N,N - dimethylaminobenzenediazonium chlorozincate	0.5
Silica	4
Polyvinyl acetate emulsion	5
Water	100

The base was dried and exposed to light under a translucent original containing opaque image areas. The exposed paper was developed by passing it through a heated chamber having temperatures of 120–150° C. A blue dye of good density and brightness was formed in the image areas of the heat developed print. The dye density was better than was obtained without the use of dextrin in the sensitizing solution.

Variations and modifications can be made in the procedures, compositions and materials herein described without departing from the scope or spirit of this invention.

We claim:

1. Two-component diazotype photoprinting material susceptible to development on heating, having on a surface of a supporting sheet, a light-sensitive layer comprising an azo coupling component, a light-sensitive diazonium compound, a neutral to acid reagent yielding an alkaline reacting compound on heating to a temperature between 100 and 200° C. and retrograded starch.

2. The article of claim 1 wherein said diazotype layer contains a pigment selected from the group consisting of alumina and silica.

3. The composition of claim 2 wherein said starch comprises an ether of starch.

4. The composition of claim 2 wherein said starch comprises an ester of starch.

5. The composition of claim 2 wherein said starch comprises dextrin.

6. A sensitizing composition for two-component diazotype printing material susceptible to development on heating, comprising an aqueous medium, an azo coupling component, a light-sensitive diazonium compound, a neutral to acid reagent yielding an alkaline reacting compound on heating to a temperature of between 100 and 200° C. and pasted starch.

7. The composition of claim 6 wherein said sensitizing composition comprises a pigment selected from the group consisting of alumina and silica.

8. The composition of claim 7 wherein said pasted starch comprises an ether of starch.

9. The composition of claim 7 wherein said starch comprises an ester of starch.

10. The composition of claim 7 wherein said starch comprises dextrin.

References Cited

UNITED STATES PATENTS

2,653,091	9/1953	Greig	96—75
2,657,137	10/1953	Kessels	96—91

2,772,974	12/1956	Kosaleck et al.	96—91
3,155,511	11/1964	Jahoda et al.	96—75
3,159,487	12/1964	Kreiger et al.	96—75
3,166,422	1/1965	McKinney et al.	96—75
3,298,834	1/1967	Eldred et al.	96—75
3,316,092	4/1967	Klimkowski et al.	96—75
3,321,310	5/1967	Fox	96—91

FOREIGN PATENTS

454,396	2/1949	Canada.
549,023	11/1957	Canada.
788,282	12/1957	Great Britain.
825,361	12/1959	Great Britain.
849,739	9/1960	Great Britain.

OTHER REFERENCES

Grant, Julius, "Hackh's Chemical Dictionary," 3rd ed., McGraw-Hill Co., New York, 1944, p. 262.

Kosar, J., "Thermal Development of Diazotype Papers," Photo Science & Eng., vol. 5, No. 4, July–August 1961, pp. 239–243.

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