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HEAT DEVELOPMENT OF DIAZO RECORDING AND COPYING PAPERS WHICH COMPRISE A QUATERNARY AMMONIUM HALIDE**Henry C. Hills, Hollis, N.H., assignor to Nashua Corporation, Nashua, N.H., a corporation of Delaware****No Drawing. Filed Apr. 28, 1961, Ser. No. 106,177
2 Claims. (Cl. 96—49)**

This invention relates to the art of image copying and reproduction and more particularly relates to the diazotype process for copying or reproducing. More specifically the present invention is concerned with a diazotype sensitized composition useful in the production of copying elements or sheets which may be exposed to the image of a graphic master and which may be subsequently developed by the application of heat.

The normal diazotype process generally comprises coating on a suitable support, usually paper, a composition containing a diazonium compound such as p-diazo-N,N-diethyl aniline- $\frac{1}{2}$ ZnCl_2 and an azo coupler compound such as 2,3-dihydroxy naphthalene-6-sodium sulfonate along with stabilizers such as thiourea and citric acid, selectively exposing the coated sensitized sheet thus prepared to radiations from a source of light of a wavelength in the ultraviolet range, and finally developing the sheet to reveal the copy of the master original. Exposure of the diazonium compound to the ultraviolet light causes this compound to become deactivated to an extent that coupling of the diazonium compound and the azo coupler compound to form the contrasting azo dye can not be accomplished at the developing stage. The resulting contrasting areas on the copy sheet generally define the image as originally impressed upon the sheet by exposure to the ultraviolet source through the graphic master. It will be apparent to those familiar with the diazotype process that by the term "develop," as used herein and in the appended claims, I do not mean the generation of image forming elements as encountered, for example, in the silver-salt photographic process, but rather the transformation of existing images from the low-contrast sensitized diazonium compound-containing coating into the high-contrast azo dye by means of the coupling reaction.

Development of the latent image impressed upon the sheet is accomplished by bringing about in the coated layer such conditions as are conducive to the coupling of the dye-forming components in the layer, for example, by causing the coated layer to become more alkaline. The necessary coupling condition is usually determined by the selected components of the diazonium/azo coupler combination. The diazotype components with which I am presently concerned are those which couple to form the azo dye under alkaline conditions and which might be referred to as "ammonia developing" compositions. With commercial diazotype sheets of the class stated the application of the alkaline medium may be accomplished by exposure of the sheet bearing the latent image to moist ammonia vapors. Other methods of obtaining alkaline conditions for the formation of the azo dyes have included the employment of alkaline solutions as in the system where the azo coupler component is applied to the sheet in alkaline solution subsequent to the exposure of the sheet-borne diazonium component to the ultraviolet light.

Basically, the diazotype system requires, for a developed image, a combination of three components; namely, (1) the diazonium compound, (2) the azo dye coupler, and (3) the alkaline developer medium. It is noted that I have here considered the dye-forming coupling reaction with respect to the substantially instantaneous rate at which it proceeds under alkaline conditions during the practical development step of the process. It will be rec-

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ognized, however, that the coupling, dye-forming reaction proceeds continuously from the moment of combining the diazonium compound and azo coupling compound, that conditions of storage such as moisture, temperature, alkalinity of coating and the like influence the rate of the coupling reaction, and that improper maintenance of such storage conditions will likely result in sufficient progress of the coupling reaction to cause a substantial development or darkening of the sheet, such being generally referred to as "pre-coupling." In order to prevent pre-coupling or formation of the azo dye prior to actual use various of the diazotype systems maintain one of the three components physically separated from the remaining components of the dye-forming combination. Such systems are similar to those previously mentioned, i.e., where the alkaline member in the form of moist ammonia vapors is separately added to the coated diazonium compound/coupler combination, or where the alkaline developer/coupler combination is added in solution to the coated diazonium compound, in both instances the complete dye-forming combination being effected subsequent to light exposure and deactivation of the diazonium compound. Other diazotype processes are known which differ somewhat from those here generally described, for example, the so-called "auto-coupling" system where the azo coupler is formed in the coated sheet by the action of light upon the diazonium compound; however, such systems will be recognized as being generally included in the basic 3-component system outlined above.

The advantages of the diazotype processes as represented by superior sharpness, density, contrast, and permanence of copy, and the ability to obtain direct positive reproductions have caused this method of copying to become widely accepted and practiced. With these obvious advantages, however, the diazotype process has introduced the less desirable requirements of maintaining dangerous and unpleasant ammonia supplies, renewing and continuously handling developer solutions, and maintaining expensive and cumbersome processing and developing equipment. The need for a simple, inexpensive, neat and effective method of developing diazotype copies has long been recognized and a number of attempts at perfecting such a method have been undertaken, but prior to my invention no thoroughly acceptable one-step process has resulted.

It has long been desired that the three basic components of the azo dye-forming reaction be incorporated in a single coating, being there held inactive until stimulated at the developing stage by exposure to a simple means of activation such as heat. Previous attempts at obtaining such a system of developing diazotype prints have been disclosed, including the incorporation of urea or its derivatives as part of the sensitized coating with the intention that subsequent to impression of the latent image heating of the sheet would result in decomposition of the urea compound with evolution of developing ammonia. This proposed practice, however, is not acceptable because of the pre-coupling resulting from alkalinity of the urea compound when applied in solution to the sensitized coating and further resulting from the instability of the urea compound during storage and in incompletely dry atmosphere. In addition, the excessively high temperatures and long development time necessary to obtain development of the image has a deleterious effect upon the copy sheet and the resulting image.

It has further been proposed to incorporate in the sensitized coating composition diazonium compounds and azo couplers which form azo dyes in a less alkaline environment than those components previously considered and additionally to add to the composition acids of low heat stability which would prevent the dye-forming coupling reaction until decomposed by heating subsequent to ex-

posure to the ultra-violet light. Instability of the stabilizing acid, low rate of coupling reaction, lack of image density, and pre-coupling in storage contribute to the unacceptability of this process. Other varied attempts to provide simple methods of effecting the coupling development of diazotype systems, primarily those based on heat initiated reactions, were found to be fraught with many of the noted disadvantages. Such disadvantages have been practically avoided by my novel development process.

An object of my invention is to provide a simple, economical, and effective means for developing diazotype copy sheets.

A further object of my invention is to provide a means for developing diazotype copy sheets without the use of unpleasant and noxious vapors or solutions.

Another object of my invention is to provide a diazotype copy sheet which may be developed by heat alone and which is stable at normal storage conditions.

Yet another object of my invention is to provide a method for preparing an economical, stable, heat-developable copy sheet which will provide clear, precise, well contrasted, and, stable copy images.

These and other objects will become apparent as this description progresses and examples embodying the principles of my invention are further outlined.

I have found that a stable, heat developable diazotype copy sheet may be prepared by coating on a suitable base sheet a sensitizing composition containing, in addition to the normal components of a diazotype coating composition, a quaternary ammonium compound such as a quaternary ammonium halide. The quaternary ammonium halide is most practically incorporated into the coating composition as a solute in the coatable mixture, but may also be applied in a top- or sub-coating with normal diazotype sensitized coatings to form a single sheet copying element. The low level of alkalinity of the quaternary ammonium halide allows such direct addition to the mixture of diazonium and azo coupler compounds without the danger of precoupling to form the azo dye. The coating composition may, therefore, be treated as the usual diazotype coating composition and the need for special precautions in coating, drying, and subsequent processing are eliminated. The stability of the quaternary ammonium halide in the dry, coated, sensitized diazotype copy sheet is such that the precoupling and loss of storage stability encountered with normal diazotype copy sheets in humid atmospheres are not increased.

The heat developable character of my novel diazotype copy sheet results from the fact that upon the application of heat the quaternary ammonium halide decomposes with the formation of a tertiary amine, the amine thereupon effectively furnishing the necessary alkalinity to promote the coupling reaction to form the azo dye. The following example will illustrate a specific embodiment of my invention.

Example 1

A coating solution is prepared in the following manner:

	Parts
Water (deionized)	360.0
Methanol	4.0
Polyethylene glycol (Dow Chemical Company Polyglycol E-4000)	48.0
Citric acid	8.0
Thiourea	20.0
Zinc chloride	20.0
Saponin	0.2
2,3-dihydroxynaphthalene-6-sodium sulfonate	7.2
p - Diazo - N - ethyl-N-hydroxyethylaniline-½ zinc chloride	6.0
Tetramethyl ammonium chloride	30.0

The coating composition thus prepared was coated on a normal 20 lb. (17 x 22-500) dry process diazotype base sheet by means of an air knife coater, the coating being metered under air pressure at 3 p.s.i.g. The coating was

dried in circulating air at about 100° F. The resulting sensitized copy sheet was exposed in the usual manner to ultraviolet light through a transparent master and the impressed latent image was developed by heating the sheet at 350° F. for about 15 seconds.

The quaternary ammonium halides of my invention are not restricted to tetraalkyl derivatives, but may additionally be selected from the aryl substituted compounds.

Example 2

	Parts
Water (deionized)	360.0
Methanol	4.0
Ethylene glycol	24.0
Citric acid	8.0
Thiourea	20.0
Zinc chloride	20.0
Saponin	0.2
2,3-dihydroxynaphthalene-6-sodium sulfonate	7.2
p - Diazo - N - ethyl-N-hydroxyethylaniline-½ zinc chloride	6.0
Trimethyl phenyl ammonium chloride	30.0

The solution was coated and coating exposed and developed as in Example 1 with similar results.

Various other quaternary ammonium halides may be used as equivalent substitutes for those shown in the examples. The use, for example, of tetramethyl ammonium iodide, tetraethyl ammonium chloride, tetramethyl ammonium bromide, tetraethyl ammonium iodide, tetrabutyl ammonium iodide, or the like will occur to those skilled in the art and the effective amounts to be used in various coating compositions will depend upon the diazo and coupler components employed and the amounts and types of stabilizers used, and may be determined by routine experimentation without the employment of any inventive skills.

It will be apparent to one skilled in the art that neither the color forming components of the examples given nor the particular stabilizers and humectants used are to be interpreted in any way as being restrictive, but rather merely representative of the various components employed in diazotype copying papers of the "ammonia-developing" type. Many useful combinations of dye-forming reactants may be employed in my novel copy sheet, among which reactants are numbered as diazonium compounds, tetrazodiphenylpiperazine-½ ZnCl₂; N,N-dimethylaniline-p-diazonium chloride-½ ZnCl₂; 4-N,N-diethylaminobenzenediazonium chloride-½ ZnCl₂; p-diazo-N-methyl-N-hydroxyethylaniline-½ ZnCl₂; p-diazo-N-ethylamino-otoluidene-½ ZnCl₂; naphthalene-2-diazo-1-oxide-5-sulfonic acid; p-phenylaminebenzenediazonium sulfate; as azo couplers, resorcinol, N-β-hydroxyethyl-α-resorcylamide, α-resorcylamide, phloroglucinol 2,3-dehydroxynaphthalene, resorcinolmonoacetate, 3-phenyl-5-methylpyrazolone, 6-hydroxy-1,2-naphthimidazole, 3-hydroxy-phenylurea, 7-methyl-4-hydroxy-2-(1)-pyridone; as stabilizers and stabilizing acids, zinc chloride, maleic acid, formic acid, phosphoric acid, tartaric acid, boric acid, and sodium-naphthalene 1,3,6-trisulfonic acid.

Specific uses of my invention are not restricted to those set forth above, for my novel compositions will suggest innumerable practical applications where heat may advantageously be employed to produce a permanent graphic record or copy. A sensitized sheet made according to my invention may, for example, be marked by means of selective application of heat as with a heated recording stylus, a heated impression plate or the like. Such sheets also lend themselves to the thermographic method of copying graphic originals which is characterized by the selective conversion of radiant energy to sensible heat in the dark portions of the graphic original. Even with such methods of impressing an image upon the sheet, i.e., by selectively heating the sensitized layer, the characteristic permanence of the diazotype process may be taken advantage of by subsequently exposing the marked sensitized

layer to ultraviolet light to effect decomposition of the diazonium compound.

As herein described by discussion and example my invention has been shown to consist not of specific formulations, but rather of a novel combination of known elements of the diazotype composition with certain quaternary ammonium compounds which I have found to be effective in producing development of the latent image upon the application of heat to the coated sheet. It is not here to be implied that the potential dye-forming combination of the diazonium compound and the azo coupler compound represents per se any part of my invention nor should the foregoing description be interpreted as restrictive of the specific elements useful in my novel combination.

I claim as my invention:

1. The method of producing permanent recordings of graphic intelligence which comprises providing a carrier sheet with a sensitized layer comprising a light sensitive diazonium compound, an azo coupler compound, and a quaternary ammonium halide, the said diazonium and azo coupler compounds being capable of reacting together in an alkaline medium to form an azo dye, the said quaternary ammonium halide being decomposable at an elevated temperature to form a tertiary amine in an amount sufficient to cause a coupling reaction between said diazonium compound and said azo coupler compound, selectively heating the said layer to a temperature in excess of the decomposition temperature of the said quaternary am-

monium halide, and decomposing the said diazonium compound by exposing the said layer to ultraviolet light.

2. The method of producing permanent copies of graphic intelligence which comprises the steps of providing a carrier sheet with a sensitized layer comprising a light sensitive diazonium compound, an azo coupler compound, and a quaternary ammonium halide, the said diazonium and azo coupler compounds being capable of reacting together in an alkaline medium to form an azo dye, the said quaternary ammonium halide being decomposable at an elevated temperature to form a tertiary amine in an amount sufficient to cause a coupling reaction between said diazonium compound and said azo coupler compound, selectively decomposing the said diazonium compound by exposing the said layer to a specific pattern of ultraviolet light, and heating the said layer to a temperature in excess of the decomposition temperature of the said quaternary ammonium halide.

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