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LIGHT SENSITIVE, HEAT DEVELOPABLE
RECORDING PAPERS

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This invention relates in general to recording papers which react to change color or react to develop color under the action of an alkaline substance, and specifically to a novel use of a compound for causing color change or development by heat in such papers.

Present application is a continuation in part to replace application 25,991 filed May 8, 1948, which is abandoned to be replaced by the present application.

An object of the invention is to provide for alkali sensitive papers, a novel method of obtaining an alkaline reaction by the application of heat.

Another object of the invention is to provide for recording papers that are sensitive to ammonia, a novel means of obtaining ammonia therefore, or at least a novel means of obtaining a reaction which is equivalent to the results obtained with ammonia.

Another object of the invention is to provide a heat sensitive paper that does not react to climatic temperatures, and requires an elevated critical temperature to cause the desired reaction.

Another object of the invention is to provide a recording paper which develops in the absence of free moisture.

Another object is to provide a method of applying a second coating to a paper having a first coating, which will react with said second coating in a common solvent, by a process which prevents reaction between two said coatings when in normal contact at climatic temperatures.

Recording papers such as are known in the art as diazo papers are useful for recording an optical image. Such papers, generally containing compounds of the azo and diazo type are sensitive to light, and when treated with ammonia and a solvent such as, generally, water, yield a highly colored compound or dye. Thus, a dye-forming intermediate or intermediate compositions such as an azo and diazo mixed composition or the like is developable to yield a colored product upon treatment with aqueous ammonia or ammonia in the presence of moisture. Now, in accordance with the present invention, a dye-forming intermediate and an ammonia-forming latent developer are coated on a backing member in mutually exclusive phases and are separately maintained thereon until the recording action.

According to one embodiment of the invention, the dye-forming intermediate compound or mixture of compounds and the latent developer are coated on the backing member in separately applied and separately maintained layers, the two reactants being excluded from a common phase throughout the entire coating operation and until each compound is stable in a separate solid phase.

According to another embodiment of the invention, the active ingredients are simultaneously or separately applied in a single layer, at least one of the reacting ingredients being maintained in a solid or crystalline phase throughout the preparation of the coated member. Such a condition is desirably attained by maintaining the one ingredient, such as, for example, the latent de-

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veloper, in its crystalline form by avoiding coating solvents or conditions which could liquefy such reactant.

As a typical illustrative example of the invention, a recording paper will be described with particular reference to a diazo type dye-forming intermediate as the color forming body and urea as the latent developer, it being understood, of course, that the scope of the invention is not to be limited thereto. A diazo coating may be placed on a paper or like backing member by a suitable method such as, for example, the method suggested in U. S. Patents 1,444,469, 1,628,279 or similar or equivalent processes. More conveniently, however, papers of such types may be obtained commercially under one or more of such commercial names as Ozalid (made by Ozalid Division of General Aniline and Film Corporation, Johnson City, New York), Multazo (made by B. K. Elliott Company, Pittsburgh, Pennsylvania) or the like.

A paper prepared by such method or obtained from such source is blasted by dry air at a temperature of about 60° C. to remove surface moisture, then coated by spraying with the following solutions:

Water	-----cc-----	100
Urea	-----grams----	20
Gelatin	-----do-----	0.5

The spraying is done, preferably, with carbon dioxide gas and a multiplicity of layers of urea are applied, each spraying accompanied with a blast of dry air heated to about 60° C. to drive off all solution possible by the time the urea reaches the coating on the paper.

Urea in a water solution will react with ammonia-vulnerable water soluble dyes at room temperatures and the urea coating must be applied in such a way as to prevent any substantial amount of reaction due to moisture present.

All chemical reactions require some time to be completed, some reactions are fast reactions and some are slow reactions and the fastness and slowness of reactions are generally referred to by the term velocity or reaction, fast reactions are high velocity reactions and slow reactions are low velocity reactions. The velocity of reaction in solution is usually very dependent upon the temperature of the solution and often upon the pH thereof.

If a urea-gelatin solute is made into a water solution of the proportions set forth herein, and this solution is coated upon commercial Ozalid or Multazo paper and the urea-gelatin solute allowed to remain in solution for one minute at a normal ambient temperature of 20° C., substantially complete development of the coating will take place. At higher temperature higher velocity of reaction takes place and development occurs in less than one minute and at lower temperatures the opposite effect takes place.

It is obviously impossible to state useful time and temperature ranges which will apply to comprehensive groups of light sensitive diazo compounds when used with different developers in the form of ureas and their derivatives under different ambient conditions.

Defining the ureas and their derivatives as developer-compounds employed in the present invention, and further referring to them as the solute, which in solution, will react with the light sensitive diazo compounds employed, a practical procedure to determine practical time and temperature ranges will be given.

The solid state critical temperature thermal decomposition reaction referred to herein, is defined as that reaction which occurs with the solute when in a solid state the solute begins to decompose by reason of its temperature having been raised to a degree at which physical or chemical decomposition takes place, such as melting, volatiliz-

ing or molecular changes. Such solid state critical temperatures are well known in the art and may be found in published works, such as for instance, *The Identification of Organic Compounds* by Neave and Heilbron, Constable & Company, Ltd., second edition, 1920. Some illustrative examples taken from this book are:

Urea, when heated above its melting point (132–133° C.), ammonia is evolved . . .

Methylurea, melts at 102° C. On heating for some time decomposes into ammonia . . .

Ethylurea, melts at 92° C. It decomposes on heating into ammonia . . .

A simple case of time determination for a simple coating at a common ambient temperature will be given as an illustrative example, but not as a limitation of the invention.

A paper support may be coated with a light sensitive diazo compound as specified heretofore or more simply a sheet of Ozalid or Multazo paper may be procured. A developer-compound is selected from the group specified herein having a solid state critical temperature thermal decomposition characteristic expressed in thermal degrees that may be attained in a practical way for decomposition thereof, and which characteristic and thermal degrees may be found in such a publication as referred to above.

Urea may be selected as a simple example. While urea decomposes with several different compounds under different conditions of thermal treatment (see *The Chemistry of Urea*, by Emil A. Werner, Longmans, Green and Company, 1923), the decomposition characteristic in the neighborhood of 150° C. is the proper temperature to employ as is obvious from the reference to this compound already given.

The urea as a solute is transformed into an aqueous solution as disclosed herein and this solution is applied to the paper already coated as disclosed above and preferably may be applied by spraying thereon. If applied to the coated paper in such a way that reaction is noted on the paper during a useful shelf-life of the paper, this means that the urea which is in this case the developer and solute of the solution, was not solidified from the solution within a time less than that required by the velocity of reaction between the solute and the first coating to react substantially, and process of applying the second coating will have to be accelerated to a such lesser time as will avoid substantial reaction between the developer-solute and the developable coating. When this time has been determined for a particular combination of developer and developable coating, a time not greater than this is the proper one to use in the employment of this invention.

In the above case with a solution temperature of 20° C. and an adequate air blast temperature of 60° C. (as disclosed herein) the solute solidifies out of the solution in about one to three seconds, and in this case no developer reaction has been observed at room temperatures over the shelf-life of the coating.

Other selected compounds may require different times and different temperatures, but the method of determining these different times and temperatures may be done by the method above outlined.

When the urea coating is properly applied there is no perceptible reaction between the urea and the dye-forming intermediate in their normal state of dryness, at climatic temperatures, over the useful life of the dye-forming intermediate, which is not impaired by the presence of the urea stratum.

The above paper with the added stratum of urea, may be exposed through a print to light in the conventional way and either developed by ammonia by the conventional method, or it may be exposed through a print to light in the conventional way to yield, in effect, a latent image and then developed by the application of a non-reactive surface (chromium for instance) heated to a temperature of about 150° C. for one minute.

No odor of ammonia is detected from this paper during or immediately after development, which is not true in the case of ammonia development, in which case the odor of ammonia comes from the paper for some time after development.

Similar recording papers have been prepared by the same methods and formulae, substituting 20 grams of either ethyl urea, methyl urea, or thiourea for the urea employed as above.

As a further advantage, the overlying urea stratum has the definite effect of increasing destruction of certain dye-forming intermediates of the diazo-azo type during exposure to light, which makes the exposure time considerably less than that required in the absence of the urea stratum.

Obviously, it is immaterial for operability of the invention whether the urea stratum is above or below the dye-forming intermediate, or whether it be mixed therewith in an isolated phase and therefore, the urea may be put on or in the paper first, and then the dye-forming intermediate applied in the same, or in an equivalent manner as described for the application of the urea stratum.

According to another embodiment of the invention, a diazo-azo composition or like dye-forming intermediate is coated on a backing member in an organic film-forming layer in an organic solvent such as a film of plastic, resin, or the like. A urea coating is applied thereto by means of a slurry in ethyl ether, in which it is substantially insoluble, whereby the film bearing the dye-forming intermediate is softened and the urea embedded therein.

As a further alternative method of forming a urea stratum on an existing stratum containing a dye-forming intermediate according to this invention comprises employing a non-aqueous solution of urea following the same method of application as was employed with the aqueous solution.

One suitable non-aqueous solution of urea for the stratum is as follows:

Methyl alcohol	-----c.---	100
Urea	-----grams---	20

To the above solution may be added 1 grm. of 326 viscosity cellulose nitrate dissolved in 6.25 c. c. of ethyl alcohol and 18.75 c. c. of ether. This solution serves as a binder and the amount of binder used may be varied to obtain the most satisfactory results sought after.

Further the cellulose nitrate seems to act as a preservative for the urea, since better shelf life is obtained when cellulose nitrate is used.

Further, when the dye-forming intermediate is not alcohol soluble, there is less tendency for the urea to react with the dye-forming intermediate during the period of application of the urea stratum.

Included within the scope of this invention are the various types of azo and diazo compounds conventionally used in light sensitive papers known as diazo papers, these generally including a diazo compound mixed with an azo coupling compound. Typically, the diazo compounds may be derived from amino-naphthols, aryl diamines, particularly those which are mono or di substituted or the undiazotized amino group or groups. Examples of commonly used diazo compounds are the diazotized amines as follows, although it is to be understood that these examples are illustrative and not limiting: p-amino-N-methyl aniline, p-amino-N-ethyl aniline, p-amino-N-ethoxy aniline, p-amino-N-dimethyl aniline, p-amino-N-diethyl aniline, p-amino-N-ethyl-N-ethoxy aniline, p-amino-N-diethyl-N-ethoxy aniline, 4-amino-2-methoxy-1-cyclohexyl aniline, 1-amino-4-(dibrom-2',6'-benzyl) aminobenzene, p-amino-N-diethyl-m-toluidine, 1-amino-3-methyl-4-ethylaminobenzene, 3-aminocarbazole, 1-amino-2-naphthol-4-sulfonic acid, and 2-amino-1-hydroxy-3,6-naphthalene disulfonic acid diazos.

Similar examples of azo coupling compounds include

the azo couplers corresponding to the following compounds, it being understood that these couplers and diazo compounds may be used in various intercombinations with each other: 2 - amino - 8 - naphthol - 3,6 - disulfonic acid, 2,3 - dihydroxy naphthalene or its 6 - sulfonic acid derivative, β - naphthol - 3,6 - disulfonic acid, 2,7 - dihydroxy naphthalene, 1,7 - aminonaphthol, 2-hydroxy naphthalene-8-biguanide, 1-amino-8-naphthol-3,6-disulfonic acid, 1-naphthol-4-sulfonic acid, 1 - naphthol - 3,8 - disulfonic acid, phloroglucinol, m-hydroxyphenylurea, acetoacetanilide, 7 - hydroxy - 1,2-naphthimidazole, 7-hydroxy naphthalene-1-biguanide and cyclohexyl acetoacet acid amide.

As an example of the employment of the invention in the making of a heat sensitive paper, such as may be used in electrical facsimile reception, the following formula is given:

Methyl alcohol	cc	100
Urea	grams	16
Mercurous chloride	do	20
Cellulose nitrate solution	cc	25

The cellulose nitrate solution is made by dissolving 2 grams of 326 viscosity cellulose nitrate in 6.25 cc. of ethyl alcohol and 18.75 cc. of ether.

To employ the above formula, the urea is dissolved in the methyl alcohol, into which the mercurous chloride is put, and then the cellulose nitrate solution is added.

The final mixture is put into a glass ball mill, with glass balls, and the mixture milled for about 75 hours, in the manner commonly used in the lacquer industry for mixing pigmented lacquer in commercial ball mills. While other methods of mixing may be employed the all-glass ball mill contains nothing that will react with the ingredients and further with round glass balls, less material is contributed from the balls to the mixture, than with flint pebbles as are sometimes used in these mills.

After milling the above mixture is coated on a suitable support, usually paper, by any suitable coating process, usually such as is used in coating photographic papers. The applicant uses the so-called "wiping process" of coating. The paper is then ready for recording by the application of heat from any source whatever, such as, for instance, a heated object or a heated stylus, or by the heat generated by a spark or by the conduction of electric current through the coating, all of which is well understood in the electrical recording art.

Recording paper properly made in accordance with the above directions, gives a pure white surface which is perfectly stable over years of shelf life. The record is intensely black and permanent.

The invention has been described most particularly with reference to urea as the latent developer, but it is to be understood that a variety of ammonia-forming compounds may be substituted therefore. Thus, urea is particularly adapted for the purposes of the present invention since it is almost infinitely stable at room temperature or slightly elevated temperatures such as are encountered during storage, reacting sharply with the ammonia developable compound at a temperature of about 150° C. Suitable equivalents for urea, possessing like advantages, are methyl urea, ethyl urea and other lower alkyl substituted ureas and similarly substituted and unsubstituted thioureas.

By the same token, the invention has been described with reference to diazo compounds such as are commonly found in commercial diazo types of recording papers, and the term "diazo compound" is used herein to refer to such type of compound. It is similarly apparent that other color forming bodies may be substituted therefore and are equivalent thereto, including for example: mercurous chloride which is blackened by ammonia; alkanin paper, which is changed from red to blue; tincture of blue hyacinth paper, which turns green; yellow fuchsine paper,

which turns red; and ammonia-vulnerable dyes, which are developed as are diazo papers.

It is presently believed that the development step according to the present invention involves an intermediate decomposition of the latent developer with the formation of ammonia as one decomposition product, which ammonia immediately reacts with the ammonia developable dye-forming intermediate. It is observed, however, that no odor of ammonia is detected during the development and, accordingly, the invention is not to be limited to the correctness of this supposition. It is further observed that the absence of ammonia odor during the development is a substantial advantage of the present invention, since the presence of this odor is a well known disadvantage of the diazo photographic process.

The term "dye-forming intermediate" as used herein describes and defines a compound which is not necessarily in itself a color body but which, upon heating with urea forms a color body or a color body of different color from the unheated compound or, upon treating with ammonia develops such new color. This term is construed to include both materials or compounds which are directly developable to a color body, such as mercurous chloride or the like, and materials or compounds capable of being thus developed after exposure to light.

The term "latent developer" as used herein describes and defines a compound substantially infinitely stable at room temperature and at temperatures below the boiling point of water, but which, when heated substantially above the boiling point of water to a temperature in the order of about 150° C. in the presence of a dye-forming intermediate according to this invention, reacts with such dye-forming intermediate to bring it to its developed color, which reaction is now understood and believed to be the result of the release of ammonia sharply at such elevated temperature.

What is claimed is:

1. The process of producing a light-sensitive heat-developable recording element, which comprises applying to a carrier a coating including a light-sensitive diazo compound and an azo coupling compound having a predetermined velocity of reaction with a solution of an ammoniate developer-compound selected from the group consisting of urea and the lower alkyl substituted ureas and said developer-compound having a solid state critical temperature thermal decomposition ammoniate reaction with said coating at temperatures substantially above solution temperatures, applying said selected compound in a solution state at a temperature substantially below said solid state critical temperature to said coating in a separate stratum, and solidifying the solute and evaporating the solvent from said solution state within a time less than that required by said predetermined velocity of reaction to appreciably ammoniate said coating in the absence of a chemical reaction-inhibitor for the coupling reaction of said diazo compound and azo coupling compound.

2. The process of producing a light-sensitive heat-developable recording element, which comprises applying to a carrier a coating including a light-sensitive diazo compound and an azo coupling compound having a predetermined velocity of reaction with an aqueous solution of an ammoniate developer-compound selected from the group consisting of urea and the lower alkyl substituted ureas and said developer-compound having a solid state critical temperature thermal decomposition ammoniate reaction with said coating at temperatures substantially above aqueous solution temperatures, applying said selected compound in an aqueous solution state at a temperature substantially below said solid state critical temperature to said coating in a separate stratum, and solidifying the solute and evaporating the water from said aqueous solution state within a time less than that required by said predetermined velocity of reaction to appreciably ammoniate said coating in said aqueous solu-

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tion state, in the absence of a chemical reaction-inhibitor for the coupling reaction of said diazo compound and azo coupling compound.

3. The process of producing a light-sensitive heat-developable diazo print, which comprises applying to a carrier a coating including a light-sensitive diazo compound and an azo coupling compound having a predetermined velocity of reaction with a solution of an ammoniate developer-compound selected from the group consisting of urea and the lower alkyl substituted ureas and said developer-compound having a solid state critical temperature thermal decomposition ammoniate reaction with said coating at temperatures substantially above solution temperatures, applying said selected compound in a solution state at a temperature substantially below said solid state critical temperature to said coating in a separate stratum, and solidifying the solute and evaporating the solvent from said solution state within a time less than that required by said predetermined velocity of reaction to appreciably ammoniate said coating in the absence of a chemical reaction-inhibitor for the coupling reaction of said diazo compound and azo coupling compound, exposing said coating with said applied solute to light under a design, and applying sufficient heat to said coating and to said solute to raise the degree of heat thereof to said critical temperature.

4. The process of producing a light-sensitive heat-developable diazo print, which comprises applying to a carrier a coating including a light-sensitive diazo compound and an azo coupling compound having a predetermined velocity of reaction with an aqueous solution of an ammoniate developer-compound selected from the group consisting of urea and the lower alkyl substituted ureas and said developer-compound having a solid state critical temperature thermal decomposition ammoniate reaction with said coating at temperatures substantially above aqueous solution temperatures, applying said se-

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lected compound in an aqueous solution state at a temperature substantially below said solid state critical temperature to said coating in a separate stratum, and solidifying the solute and evaporating the water from said aqueous solution state within a time less than that required by said predetermined velocity of reaction to appreciably ammoniate said coating in said aqueous solution state in the absence of a chemical reaction-inhibitor for the coupling reaction of said diazo compound and azo coupling compound, exposing said coating with said applied solute to light under a design, and applying sufficient heat to said coating and to said solute to raise the degree of heat thereof to said critical temperature.

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