

March 1, 1966

R. D. MURRAY ETAL

3,238,047

DATA PROCESSING MEDIA

Filed Aug. 20, 1962

3 Sheets-Sheet 1

Example No.	Source of Metal Ion	Parts by Weight	Source of Sulfide Ion	2nd Source of Metal Ion	Solvent
	All Parts By Weight				
1	Lead nitrate	10.0	Ammonium thiosulfate 22.3 6-72	Ferrrous sulfate Heptahydrate Cobalt sulfate Heptahydrate Nickel sulfate Hexahydrate	Water 60.4
2	Lead nitrate	4.5	12.1 3-36	7.6 0.5-20	75.8
3	Cupric sulfate pentahydrate	5.5 2.5-30	12.0 3-36	7.5 1.0-30	75.0
4	Cupric sulfate pentahydrate	4.9	7.4 1.5-30	5.5 1-15	78.0
5	Cupric sulfate pentahydrate	7.7	22.8 6-72	8.1 1-16	61.4

TABLE A

FIG. 1

INVENTORS

Richard D. Murray
Elliot Berman

March 1, 1966

R. D. MURRAY ETAL

3,238,047

DATA PROCESSING MEDIA

Filed Aug. 20, 1962

3 Sheets-Sheet 2

Example No.	Source of Metal Ion	Source of Sulfide Ion	2nd Source of Metal Ion	Additive	Solvent	pH
	All Parts By Weight	Parts by weight				
6	Cupric sulfate pentahydrate	5.4 16.1 8-64	6.1 1-12	Potassium acid phthalate Sodium bisulfite Ammonium hydroxide Halopont Blue BXM Thiourea	70.0	4.0 2.5-7.0
7	Cupric sulfate pentahydrate	5.37 15.92 8-64	8.45 0.5-16		68.90	3.75 2.5-7.0
8	Cuprous chloride	2.11 15.06 8-64	8.87 0.5-16		72.54	4.5 2.5-7.0
9	Copper-thiosulfate complex	5.04 11.90 8-64	8.94 0.5-16		73.02	4.0 2.5-7.0
10	Copper-thiosulfate complex	4.89 11.56 8-64	8.69 0.1-16		73.45	4.5 2.5-7.0

FIG. 2

TABLE B

INVENTORS

Richard D. Murray
Elliot Berman

March 1, 1966

R. D. MURRAY ETAL

3,238,047

DATA PROCESSING MEDIA

Filed Aug. 20, 1962

3 Sheets-Sheet 3

--Example number	Metal Salt Complex	All Parts By Weight	Complex parts by weight	Thermal-Acid-Providing Ingredient															Solvent
				Ammonium bisulfate	Semicarbazide Hydrochloride	Malonic Acid	Zinc fluoroborate 40% solution	4-amino-1-naphthol hydrochloride	2-3-dimethylaniline Hydrochloride	Oxalic acid	Ammonium formate	Malic acid	Ammonium sulfate	Zinc fluoroborate	Ammonium nitrate				
11	Copper-thiosulfate complex		14.65	2.00 1-10													Water	83.35	
12	Copper-thiosulfate complex		14.76		1.83 1-10													83.41	
13	Copper-thiosulfate complex		14.99			1.66 1-8												83.35	
14	Copper-thiosulfate complex		13.16				3.49 2-15											83.35	
15	Copper-thiosulfate complex		11.17				2.99 1-15	2.49 1-13										83.35	
16	Copper-thiosulfate complex		11.49				3.09 1-15		2.07 1-10									83.35	
17	Copper-thiosulfate complex		11.5							1.6 0.5-10								83.35	
18	Copper-thiosulfate complex		11.5								1.0 0.5-12							83.35	
19	Copper-thiosulfate complex		11.5									1.7 1-10						83.35	
20	Copper-thiosulfate complex		11.5										1.6 1-12					83.35	
21	Copper-thiosulfate complex		11.5											1.0 0.5-6				83.35	
22	Copper-thiosulfate complex		11.5													1.0 0.5-7		83.35	

TABLE C FIG. 3

INVENTORS
Richard D. Murray
Elliot Berman

1

3,238,047

DATA PROCESSING MEDIA

Richard D. Murray, Roslindale, and Elliot Berman, Braintree, Mass., assignors to Ittek Corporation, Lexington, Mass., a corporation of Delaware

Filed Aug. 20, 1962, Ser. No. 217,837

11 Claims. (Cl. 106—21)

This application is a continuation-in-part of our co-pending application, Serial No. 70,545, filed November 21, 1960, now abandoned.

The present invention relates generally to novel thermally responsive graphic data processing materials, and to novel sensitizing compositions therefor.

More particularly the invention relates to novel compositions to be applied to a carrier for forming colored images on a suitable carrier material capable of being thermally sensitized to reproduce a graphic original by thermally responsive marking and to the combinations of such compositions and carriers as articles of manufacture. Such carrier material may be paper, cloth, cellulosic compositions, for example, or other suitable web or sheet-like materials. The instant invention presents improvements over the fixable thermally responsive graphic materials disclosed in co-pending U.S. application, Serial No. 70,741, of Leonard E. Ravich, filed November 21, 1960 and assigned to the assignee of the present application.

Prior materials, such as thermographic copy papers and the like, except for those disclosed in said Ravich application, have certain varying and differing disadvantages and undesirable limitations. A few of these disadvantages are that the image formed, when a sensitized carrier is exposed to heat, may be blurred, of poor or non-uniform color intensity and/or provide poor contrast with the carrier; moreover, image formation may require heating for an undesirably long time period. Such carriers in some instances are sensitized by compounds in a wax layer, but such wax layer carriers are relatively expensive to manufacture; yield poor image resolution, and the image formed may subsequently be obscured by exposure of the carrier to further heat or radiation. In the Ravich application, systems are disclosed and claimed in which a permanent thermographic image is formed on a carrier and the latter is thereafter desensitized in the unreacted areas thus rendering the carrier incapable of further image obscuring color changes due to heat. The present invention also provides permanently fixable carriers falling within the purview of the Ravich disclosures with improvement of the quality of the carrier materials and images produced, obviates the above-mentioned disadvantages of prior papers, and has the following generally advantageous properties: black print on white background; inexpensive system; aqueous solution for simplified manufacture; paper support or carrier not adversely affected; good stability under normal storage conditions; stable to ultraviolet radiation, e.g., sunlight, for a prolonged duration; will not smudge; print is of archival quality; good sensitivity, i.e., it does not require a high temperature or a relatively long time at a specific temperature, or heating over a wide range of temperature to produce a visible change of sufficient intensity; can be used as a master for the reproduction of thermographic prints; capable of producing images of good color intensity, sharp detail in the letter outlines, with no burn-out and spread of letter outlines; may be used to copy any original without degrading the original, so as to permit repeated use of the original; satisfactory copies are produced when subjected to relatively widely varied quantities of radiant energy; not oversensitive to impurities;

2

and completely fixed, including rendering background no longer thermally sensitive, by water rinse, among others.

Briefly the present invention involves the formation of inorganic pigments, such as metal sulfides, by the action of heat on a formulation comprising sources of metal ions and sulfide ions, the metal ions being capable of forming a colored sulfide. As one aspect of this invention, it has been discovered that by the use of a combination of different metal ions and a source of sulfide ion, a synergistic effect is obtained which results in thermographic prints possessing contrast, sensitivity, and print color that are superior.

It has also been discovered, in accordance with the present invention, that certain agents may be employed in the sensitizing compositions to improve the printing ability, print stability, and background stability of sensitized carriers.

A further feature of this present invention resides in the discovery that the thermal sensitivity of certain compounds in a sensitizing composition may be improved by the addition of acidic or thermally responsive acid producing materials. These compositions may be of the type wherein ions of a single metal form the inorganic pigment.

The use of a source of sulfide such as thiosulfate, for example, and metal ion to produce images by application of heat thereto has been suggested in British Patent Nos. 282,759 and 318,203. In both patents, a metal salt such as nickel nitrate reacts with another compound by application of heat to form dark-colored compounds such as oxides, hydroxides, sulfides or halides. The metal salt as disclosed in the latter patent is mixed with adhesive substances, solvents, oxidizing agents and sulphur compounds. In examples illustrating the invention, nickel nitrate is mixed with sodium thiosulfate, and sodium nitrite or nitrate is added; however, the addition of the sodium nitrite or nitrate differs markedly from the present invention because it is used as an oxidizing agent and the sodium ion does not enter into the actual color forming reaction products with the sulfide and nickel ions. Therefore, an ion from a single metal forms a colored metallic sulfide, whereas in the present invention a synergistic reaction is obtained by use of a combination of two different metal ions thereby providing results superior to such prior compositions.

U.S. Patent Nos. 2,637,657; 2,663,655; 2,740,896 and 2,813,042 also employ metallic salts and sulfur compounds to produce an image by heat, but in each case the involved concept differs from the concept of combining two different metal ions with a source of sulfide ions as is characteristic of certain embodiments of the present invention. For example, in U.S. Patent No. 2,637,657 plural metal salts are used, but one of the salts is used in relatively small quantities and for the purpose of providing heat by exothermal decomposition at low temperatures to catalyze the decomposition of the other image producing salt. The final recording by this process consists of a combination of metals and/or suboxides of the metals in dark contrast to the unaffected white metal salts used.

In U.S. Patent No. 2,633,655, two different metal compounds, one being an alkaline earth metal sulfide and the other being a heavy metal salt, are applied to a copy paper and are physically prevented from reacting with each other by a film forming binder material. Heat applied to a copy carrier treated with such a sensitizing composition reduces the strength of the binder, and permits the reactants to form a colored image. In this reaction, however, the heavy metal salt and sulfide react in a direct ion-exchange electron acceptor-donor chemical

reaction to form a colored sulfide of the heavy metal only, and the alkaline earth metal does not participate in the formation of the colored image.

In U.S. Patent No. 2,740,896, two different metallic salts are mixed with ammonium thiosulfate, but the salts have the same metal ion (nickel) rather than having different metal ions, or at least, different metals, as is necessary in accordance with certain features of the present invention to achieve the synergistic reaction.

U.S. Patent No. 2,813,042 also discloses that a single metal salt and a sulfur compound will form a colored image, that this thermal reaction can be catalyzed by the addition of alkali metal salts of low aliphatic acids, and that small amounts of inorganic polyvalent salts such as magnesium chloride may also be added to catalyze and improve the development of background colors. Inasmuch as a single metallic salt is involved in the actual color changing reaction, the copy papers disclosed in this patent also differ from the present invention.

In the thermographic copying process as it is usually practiced at the present time, a graphic original is placed in surface contact with a copy sheet, and the original is then irradiated with infrared radiations that are directed through the copy sheet. The radiation is absorbed by the dark areas of the original and is converted to heat. The heat causes a color change to occur in the copy sheet, to form a reproduction of the original. Typically, the copy paper temperature is raised, during copying to about 65°-75° C. in the non-image areas, and to about 95°-115° C. in the image areas. Thus, a basic requirement of a good image-forming system is that it forms a high density visible marking or discoloration, at about 110° C. in a relatively short time period, while having no noticeable or material change at about 70° C. in this same period. Moreover, the system must be stable during a reasonable length of time at 20°-25° C., to permit normal handling and storage prior to use.

At present, the thermal copying papers that are widely used meet these temperature requirements by utilizing physical means to prevent any change except at copying temperatures. Usually, this involves the use of a carefully selected wax that melts and flows at copying temperatures, either to bring together chemicals that react to make a colored reaction product, or to flow to effect a change in transparency, with a blushed layer of lacquer that is adjacent the wax.

One serious problem with thermographic systems that rely upon a wax is the bleeding of images and general smearing that may occur when the paper is overheated.

It is an object of the invention to provide improved data processing media for use in thermally responsive marking processes.

A further object of the present invention is to provide improved thermally responsive graphic data processing media providing improved thermal sensitivity.

Yet a further object of the present invention is to provide thermally responsive graphic data processing media providing improved marking color density and contrast.

Another object of the present invention is to provide improvements in thermally sensitized graphic carrier materials for thermally responsive marking processes, and in sensitizing compositions capable of producing images of excellent quality without harmfully affecting the carrier and capable of being desensitized when treated with a suitable solvent.

A further object of this invention is to provide a novel thermographic sensitizing solution for forming metal sulfide images on thermographic copy carriers having a source of sulfide ions and two sources of different polyvalent metal ions which may, for example be two heavy metal salts or a metal salt and a metal salt complex.

Still another object of the present invention is to provide copy carrier materials with novel sensitizing compositions having as essential ingredients two different

sources of heavy polyvalent metal ions and a source of sulfide ion or a metal salt complex, and an additive providing acid at an elevated temperature.

A more specific object of the invention is to provide a heat-sensitive copying paper, for use in the thermographic copying of heat-absorbing graphic materials, that is relatively inexpensive and that can produce high quality reproductions.

A related object of the invention is to provide a copying paper of the character described that has good shelf life together with satisfactory sensitivity for use in thermographic copying.

Another object of the invention is to provide a heat-sensitive copying paper for use in thermography, that is characterized by good paper physical properties, reasonable cost, and permanence of the reproduction that is formed.

A further object of the invention is to provide a thermal copying paper that is thermally sensitized by an applied chemical composition that is impregnated in the paper while in solution, and that is visibly reactive in response to thermographic copying temperatures.

A related object of the invention is to provide a copying paper of the character just described, in which the copying paper is stable at normal room temperatures and at the background temperatures that are encountered in the thermographic copying process, by reason of the chemical constitution of the sensitizing composition.

Further objects and advantages of the present invention will become apparent from the appended claims, the following description, and from the accompanying drawings wherein the FIGURES 1, 2 and 3 contain three tables (A, B, C respectively) of examples of sensitizing compositions fixable by a solvent rinse.

In accordance with the present invention, compositions are provided which when heated form a colored metallic sulfide from two metal ions, each capable of forming a colored sulfide alone, or from a complex compound embodying such a metal ion and a source of sulfide ion. Temperatures on the order 110° C. or above will be sufficient to form the sulfide.

Each type of the compositions described below is fixable after exposure to an image forming process. By application of a suitable solvent rinse (water is preferred) to the carrier material, the background areas are rendered incapable of thermographically forming an image. Therefore, with the permanent images formed in selected heated areas and an irreversibly desensitized background, the exposed carrier has a fixed image, with respect to permanency of image and permanency of background thereon, which may be stored indefinitely or used as a master for thermographic reproduction of further copies by thermographic or in other processes such as the ozalid-type.

In each case, the images thermally formed with the compositions of the present invention are essentially insoluble, particularly in water. This is in contrast to the residual background, which may be rendered thermally non-responsive to cause further color change by solvent removal of one or more of the active color forming ingredients. The insoluble metal sulfide colored image on the carrier provides copies of substantially archival quality in that they are stable under ambient temperature, humidity and light conditions.

In FIGURES 1, 2 and 3 each box of the tables lists the relative proportions of ingredients under a broad classification thus making up examples which are read horizontally from the particular example number. The uppermost figure above the dotted line in each box represents a specific amount of ingredient which has been found to be particularly effective while the lower figures represent ranges of the preferred amount of the particular compound which will give highly effective results. The amount of solvent indicated can be increased to give any dilution desired. The ranges are of preferred amounts and are not to be construed as limitative in any respect.

5

In Table A are given examples of specific compositions which have been found to yield a synergistic effect in forming thermographic images due to the use of a combination of metal ions with a sulfide ion. The metal ions are generally supplied by metallic salts of heavy polyvalent metals. These examples illustrate preferred compositions and preferred relative amounts of ingredients.

The quantities given in the examples may be varied over a wide range. In general the sources of metal ions may be present in any relative proportions; however, the preferred range is from one to twelve times the weight of the other. To illustrate, in Example 3, the amount of cupric sulfate is varied from 2.5–30.0 parts by weight, the ammonium thiosulfate from 3.0–36.0 parts by weight, the ferrous sulfate from 2.5–30.0 parts by weight, and water as required to provide an aqueous solution.

In Table B are given examples which illustrate how, in accord with the present invention, the stability and thermal sensitivity of heat sensitizing formulations may be controlled by regulating the pH and other factors of the system. It has been found that the most satisfactory results are obtained in the pH range of from 2.5 to 7.0 inclusive. These properties may be improved by the addition of a buffer, as for example, potassium acid phthalate. Increased solution stability is also obtained by the addition of a reducing agent, referred to in the claims as an additive, as for example sodium bisulfite, the addition of an anti-oxidant, as for example thiourea; or the substitution of a "less-sensitive-to-oxidation" source of ferrous ion which may be ferrous ammonium sulfate for example.

The following specific example, Example 6, Table B, of another composition in accord with the present invention is used to illustrate a procedure that may be used for the preparation of the sensitizing solutions.

Example 6

Ingredients	Parts by Weight Preferred	Range
Cupric sulfate, pentahydrate.....	5.4	-----
Ferrous sulfate, heptahydrate.....	6.1	-----
Ammonium thiosulfate.....	16.1	-----
Potassium acid phthalate.....	1.4	0 to 8.0
Sodium bisulfite.....	0.7	0 to 5.0
Ammonium hydroxide.....	0.3	-----
Water.....	70.0	-----

The pH of the solution is maintained above 4.0 throughout the preparation by the addition of ammonium hydroxide if necessary. The ammonium hydroxide, sodium bisulfite, potassium acid phthalate and ammonium thiosulfate are dissolved in the water at room temperature with stirring. The cupric sulfate is then added with stirring until the blue initial color is discharged. The ferrous sulfate is added and finally after all salts are dissolved the pH of the solution is adjusted to 4.0 with ammonium hydroxide and/or dilute sulfuric acid. The solution is then ready for application on or in the desired carrier material. The carrier may be dried at room temperature or any elevated temperatures provided that the sensitized carrier temperature does not exceed 60° C.

While description thus far has been with primary reference to the preferred metal ion supplying compounds such as lead nitrate, cupric sulfate, ferrous ammonium sulfate, etc., other similar metallic compounds capable of forming a colored metal sulfide or other colored reaction product may be used, e.g., metallic compounds of mercury, antimony, manganese, tin, bismuth, arsenic, and cadmium. As the color of the sulfide of these individual metals may be yellow, orange, pink or in general, other than black, they nevertheless may produce readily discernable colorations on a copy carrier, particularly in combination with other metal compounds as used heretofore if the latter is tinted by a contrasting color.

Other examples employing addition agents for improv-

6

ing print and background stability, and printing ability are given in Table B, Examples 7 and 8.

Heavy metals as used in the specification and claims means those metals having an atomic number greater than 21.

By utilizing two different heavy polyvalent metal ions in the same sensitizing composition it has been discovered that remarkably improved images may be formed on a carrier. As noted the improvement provides several advantages. While it is not known what causes the synergistic effects of the present compositions, it has been determined that the results of using a combination of metal ions in color intensity, contrast, and thermal sensitivity are superior to the results obtainable by using the metals individually and adding their individual results together.

Further, although the anion associated with the metal ion and the cation associated with the thiosulfate is specified, virtually any equivalent source of thiosulfate will suffice. For example, rather than using ammonium thiosulfate, any of the alkali metals could be substituted in an equal molar amount for ammonium. Thiosulfate compounds used throughout this specification have been found to react in a manner far superior to other sources of sulfide ion. Similarly, in place of nitrate or sulfate serving as the source of metal ion, any of the halides could be substituted.

It has also been discovered in accordance with the present invention that a metal salt complex may be utilized as a source of metal and sulfide ions.

The following description illustrates the use of complex compounds as exemplary of this discovery wherein a copper-thiosulfate salt complex may be used. The cupric sulfate or cuprous chloride in formulations such as in Examples 7 and 8 may be replaced by a complex compound, which may be prepared as follows:

250 grams of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ is dissolved in 1160 ml. of water and the solution filtered. 444.6 grams of ammonium thiosulfate is dissolved in 340 ml. of water and the solution filtered. The thiosulfate solution is added to the cupric sulfate solution with stirring, 360 ml. of acetone are added, the solution is cooled to 9° C. filtered, partially air dried, washed with 60 ml. of denatured alcohol and air dried. The yield is 278 grams of the complex.

The preparation of additional suitable copper thiosulfate complexes is disclosed by G. Spacu and I. G. Murgulescu in the Bull. Soc. Sc. Cluj., V (first part) pages 61–107 (Nov. 22, 1929) pages 254–272 (Apr. 28, 1930) pages 344–370 (Nov. 15, 1930) and (second part) pages 85–107. The use of this preferred complex is illustrated by Examples 9 and 10 of Table B.

In Example 10 of Table B in FIGURE 2, the range of ferrous ammonium sulfate may be extended to 0 for certain applications where thermal sensitivity is not a critical requirement. Similarly ammonium thiosulfate may be eliminated and the composition will still retain its thermally responsive marking or color forming ability.

The Halopont Blue BXM is an example of a dye which may be added to the above formulation that improves both the image and background appearance.

Another discovery in accord with the present invention resides generally in increasing the thermal sensitivity of a complex metal salt compound wherein the complex is formed from a metal ion and thiosulfate by the addition of thermally acid producing materials.

Thus, the previously described copper-thiosulfate complex may be used in sensitizing compositions in the absence of other metal ions with increased thermal sensitivity if acidic or thermal-acid-producing additives are present. Broadly salts of weak inorganic or organic bases and strong acids, with or without added zinc fluoroborate, and carboxylic acids, are satisfactory. Examples of these compositions are given in Table C.

In all of the above examples, the copper-thiosulfate complex is preferably purified to remove impurities which could possibly cause background discoloration.

The relative amounts of materials are not critical, the thermal sensitivity generally improving with increased amounts of acid or acid-former. Thus, the thermal sensitivity of the above compounds may be controlled as desired to adapt a carrier for various thermally responsive marking processes and machines now commonly used, to duplicate with optimum results by varying the amount of acid or acid-former, the thermal sensitivity improving with increased amounts thereof.

In general the sensitizing compositions of this invention are applied to carrier materials in solution with a suitable solvent such as water. The solvent is employed for practical purposes inasmuch as it provides easy uniform application of the compositions to the carrier. When the carrier to which the solution has been applied is dried, the solvent is no longer present. Thus, it will be apparent to those skilled in the art that the amount of solvent employed with the compositions is not an important factor affecting formation of an image.

Suitable carrier materials include paper, cloth and sheets or films of natural and synthetic materials or combinations thereof. Any carrier to which the sensitizing compositions can be applied satisfactorily can be utilized. The compositions of the present invention are normally applied to the carrier materials in amounts sufficient to deposit solids in quantities ranging from 1 to 10 pounds per 3000 sq. ft. of carrier surface, dry basis.

Example 23

The composition of Example 6 was applied to a web of white paper stock by a dip-squeeze process and the impregnated paper was allowed to dry at room temperature. The dried sheet was white in color, but became black in color when heated to 100° C. for less than three seconds.

Example 24

Thin white greaseproof paper was passed through an aqueous solution of the composition of Example 10. The paper was dried and found to have picked up about 6 pounds of the composition solids per 3000 sq. ft. of paper. The white color of the impregnated paper was found to be unchanged upon prolonged exposure to sunlight. The paper formed clear, sharp black image areas against a white background on heating in the thermographic copying process.

It has also been discovered that cuprous oxide is a particularly desirable source of copper in the sensitizing solution. Cuprous oxide is stable, inexpensive, and readily available. It is surprising that cuprous oxide can be employed in the compositions of the present invention, since it is characterized by very low solubility. However, it has been discovered that cuprous oxide is very soluble in ammonium thiosulfate solutions, and accordingly, cuprous oxide can be used in the sensitizing compositions of this invention that contain ammonium thiosulfate.

One purpose in preparing the complexes previously described herein was to provide a source of cuprous copper without also producing some tetrathionate material (the oxidation product of thiosulfate). The sensitizing compositions of this invention are intended to provide a source of cuprous copper since copper salts ordinarily provide such a source in the presence of thiosulfate ion.

In applying the thermally sensitive compositions of this invention to a web to make a thermographic paper, the sensitizing solution can be applied in any convenient manner to the paper web, but roll coating is preferred for ease of application. The concentration of the solution that is employed can be varied over a wide range, from a heavy dispersion to a dilute solution. Moreover, the sensitizing composition may be applied in such form that it will form a surface coating primarily, but preferably, it is applied in aqueous solution directly to an absorbent paper web so that impregnation occurs and

the solution is applied not only to the surfaces of the web but also throughout at least a substantial part of its thickness.

The amount of the sensitizing solution that is applied to the web, on a dry basis, is important in connection with the quality of the copies that can be obtained. In applying the sensitizing composition, the amount of the solution that is applied and its concentration should be regulated so that the amount of solids applied is in the range between about 3.5 pounds and about 6 pounds per ream (3000 sq. ft.), dry basis. When the weight is 4 pounds per ream or less, the print tends to be light; the lighter the applied weight of sensitizing composition solids, the lighter the print. A preferred range is from about 4.5 pounds per ream to about 5.5 pounds per ream. When the weight is above about 6 pounds per ream there is some tendency for thermographic paper to pick up water, which is undesirable for this application.

For the production of a thermographic paper of desirable characteristics, the base paper that is selected for coating with the sensitizing solution preferably should have a weight in the range between about 21.0 and 24.0 pounds per ream, and preferably, 22.0 pounds to 23.0 pounds per ream, with a brightness reading on the photovolt scale in the range from about 79.0 to about 85.0 and preferably in the range from 80.0 to 84.0, with high infrared transmission, and with single sheet opacity, as measured on the Bausch & Lomb scale, in the range from about 60.0 to about 66.0, and preferably in the range from 61.0 to 65.0.

After the paper web has been sensitized by the application of the sensitizing solution, and has dried, it is preferred that a moisture barrier be applied on both surfaces of the paper web, in order to maintain the moisture level of the sensitized paper substantially constant. While a wide variety of materials may be employed to form the barrier coating, paraffin wax is preferred because of its ready availability and because of the simplicity of application. For example, up to about 0.5 pound per ream of paraffin wax may be applied from a dilute solution of the wax in toluene or some other suitable solvent. A preferred amount of wax, applied on both surfaces of the paper web, is about 0.20 pound per ream, although the amount applied may be modified over a wide range, depending upon the physical characteristics of the thermographic paper that are desired.

Many other film forming materials, that will resist change in the moisture content of the thermographic paper, can be used instead of wax, such as, for example, many of the common rubber base coatings that are now used as coatings in the paper industry, and synthetic plastic coatings of the same type, such as, for example, the many polyethylene coatings that are commonly used on papers.

It has also been discovered that the incorporation of a polyol, such as glycerine, in the sensitizing compositions of this invention affords improved and desirable results. For example, after a sensitizing solution has been prepared that includes a substantial amount, greater than about 5% by weight, of glycerine, it is found that the stability of the solution is improved, and that the physical characteristics of the paper, after the application of the solution, are modified in a desirable way so that the paper becomes very pliable, has a higher fold endurance, and will not become embrittled. Moreover, the presence of glycerine produces an apparent improvement in printing speed, and in many cases, assists in controlling the moisture content of the sensitized paper, since the glycerine content will ordinarily help maintain a lower moisture content in the paper, up to certain relative humidities in the atmosphere, than would be the case in the absence of glycerine.

While glycerine is the preferred polyol, other polyols can be employed with similarly beneficial results. For example, many of the lower molecular weight polyethylene glycols can be used rather than glycerine.

In general, in preparing the sensitizing solutions in accordance with this invention, it is preferred that the ratio of copper to thiosulfate ion, in terms of mols, be in the range from about 0.075 to about 0.35, to 1, and preferably in the range from about 0.15 to about 0.25, to 1. Similarly, the ratio of copper to ferrous iron, in terms of mols, should be about 36 to 1, and preferably should be in the range from about 15 to 9, to 1. Moreover, the pH of the composition immediately prior to its application of the carrier material, should be in the range between about 2.5 and 7.0, and preferably, close to about 5.5.

The invention will now be described in further detail by reference to additional specific examples that disclose the procedure for preparing sensitizing compositions in accordance with other preferred embodiments of the invention and including the application of these compositions to suitable carrier materials. Reference to "parts" hereafter are to parts by weight.

Example 25

A sensitizing composition was prepared by dissolving 250 parts of ammonium thiosulfate in 500 parts of demineralized water. Thereafter, twenty parts of cuprous oxide was added slowly while the solution was stirred rapidly. During the addition of the cuprous oxide, the pH of the solution was continuously maintained in the range between about 2.5 and 10.0 by adding small quantities of adipic acid, as needed. When the cuprous oxide addition was completed, 100 parts of ferrous ammonium sulfate hexahydrate was added. The pH was adjusted to 5.6 with adipic acid, and the solution was filtered to remove any undissolved material.

The resulting solution was colorless. It was applied to a white paper web, and the web was then dried at room temperature.

The sensitized paper was found to develop clean, sharp images when used in the thermographic process. When tested by heating at 120° C. for 0.25 second, the paper developed a green-black coloration.

Example 26

A sensitizing solution was prepared by adding 44 parts of ammonium thiosulfate and 9.8 parts of glycerine to 43 parts of demineralized water. This mixture was stirred, and 3.2 parts of cuprous oxide were added slowly as the mixture was stirred, until all of the cuprous oxide had dissolved. Thereafter, 16 parts of ferrous ammonium hexahydrate was added. The pH was then adjusted to 5.8 with adipic acid. The solution was then filtered and roll coated on 27 pound opaque, white greaseproof paper.

The sensitized paper discolored to a dense green-black upon heating to 110° C. for one second.

Example 27

The sensitized paper of Example 26 was coated with a protective wax film by roll coating on the paper a 1½% solution of paraffin wax in toluene. The solvent was permitted to evaporate at room temperature. The amount of wax applied was about 0.20 pound per ream. The thin wax barrier coating was found to be effective in extending the shelf life of the sensitized paper.

In preparing the sensitizing solutions, the pH may be maintained within the preferred range of 2.5 to 10 through the use of any convenient and compatible material. Ordinarily, ammonia is most convenient when a basic material must be employed. When an acid is used, many organic and inorganic acids can be employed. Among the most satisfactory are the water soluble dicarboxylic acids such as, for example, adipic, glutaric, and the like. Adipic acid is particularly suitable because it is odorless, soluble in water, and does not form any undesirable complexes with the components of the compositions.

While the invention has been described with particular reference to thermographic paper, broader applications of the sensitizing compositions are contemplated. The carrier material for the sensitizing compositions of this invention preferably is cellulosic paper, but may be paper made from other materials, and, as well, may be cloth, or sheets or films of natural or synthetic materials or combinations thereof.

The invention may be embodied in other specific forms without departing from the spirit or essential characteristics thereof. The present embodiments are therefore to be considered in all respects as illustrative and not restrictive, the scope of the invention being indicated by the appended claims rather than by the foregoing description, and all changes which come within the meaning and range of equivalency of the claims are therefore intended to be embraced therein.

What is claimed and desired to be secured by United States Letters Patent is:

1. In a heat sensitive copy medium for the reproduction of images in thermographic processes, said medium comprising a substrate and an image forming composition including a combination of thermally responsive chemical substances, said composition being an integral part of said medium so that upon the application of heat in a selected pattern to said medium, a visible image of the colored reaction products of said chemical substances is formed in a pattern conforming to that applied to said medium, the improvement wherein said combination of thermally responsive chemical substances consists essentially of a thermally responsive substance comprising copper ion, a thermally responsive substance comprising ferrous ion and a thermally responsive substance comprising thiosulfate ion.
2. The heat sensitive medium of claim 1 wherein said substance comprising copper ion contains said ion in the form of cuprous ion.
3. The heat sensitive medium of claim 1 wherein said substance comprising a copper ion is cuprous oxide.
4. The heat sensitive medium of claim 1 wherein said image forming composition includes a polyol.
5. The heat sensitive medium of claim 1, wherein said image forming composition includes glycerine.
6. The heat sensitive medium of claim 1, wherein said image forming composition includes glycerine in an amount equal to at least five percent by weight of said image forming composition.
7. The heat sensitive medium of claim 1 wherein said medium is coated on each of its surfaces with a moisture resistant barrier coating.
8. The heat sensitive medium of claim 7, wherein said barrier coating consists of paraffin wax.
9. In the process for producing a heat sensitive copy medium from the reproduction of images in thermographic process involving the steps of applying an image forming composition to a substrate, said composition including a combination of thermally responsive chemical substances so that the application of heat in a selected pattern to that portion of said substrate containing said composition results in the formation of a visible image of the colored reaction products of said chemical substances, the improvement which comprises including in said composition as the combination of thermally responsive chemical substances thereof, a thermally responsive substance comprising copper ion, a thermally responsive substance comprising ferrous ion and a thermally responsive substance comprising thiosulfate ion.
10. The process of claim 9 wherein said image forming composition is applied to said substrate in the form of a substantially colorless solution, said solution consisting essentially of

250 parts by weight of ammonium thiosulfate,
500 parts by weight of a demineralized water,
20 parts by weight of cuprous oxide,

11

100 parts by weight of ferrous ammonium sulfate hexahydrate and sufficient amounts of adipic acid to adjust the pH of the solution to a value of substantially 5.6.

11. The process of claim 9 wherein said image forming composition is applied to said substrate in the form of a substantially colorless solution, said solution consisting essentially of

44 parts by weight of ammonium thiosulfate,
9.8 parts by weight of glycerine,
43 parts by weight of demineralized water,
3.2 parts by weight of cuprous oxide,
16 parts by weight of ferrous ammonium hexahydrate and sufficient adipic acid to adjust the pH of said solution to a value of substantially 5.8.

12**References Cited by the Examiner****UNITED STATES PATENTS**

1,693,735	12/1928	Warga et al.	117—3.2
1,763,291	6/1930	Brookby	8—3
2,625,494	1/1953	Morrison.	
2,637,657	5/1953	Ozols	106—19 XR
2,813,042	11/1957	Gordon et al.	117—36.8
2,864,720	12/1958	Maguire et al.	106—31 XR
2,999,035	9/1961	Sahler	117—36.8

FOREIGN PATENTS

552,743 2/1958 Canada.

ALEXANDER H. BRODMERKEL, *Primary Examiner.*

MORRIS LIEBMAN, *Examiner.*