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METHOD OF MAKING A HEAT-SENSITIVE COPY-SHEET AND RESULTANT ARTICLE

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FIG. 1

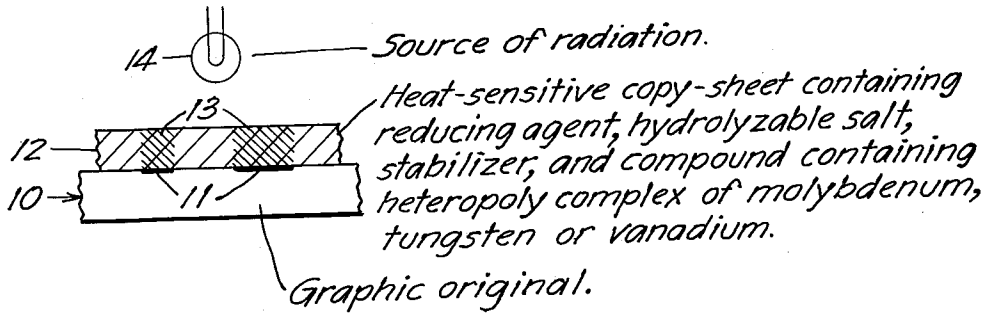
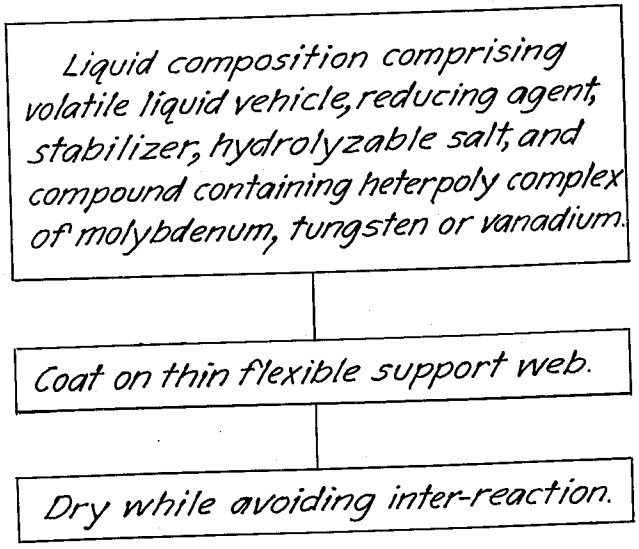


FIG. 2



INVENTOR

DONALD L. THOMSEN

BY

Carpenter, Abbott, Coulter & Kinney

ATTORNEYS

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METHOD OF MAKING A HEAT-SENSITIVE COPY-SHEET AND RESULTANT ARTICLE

Donald L. Thomsen, White Bear Lake, Minn., assignor to Minnesota Mining and Manufacturing Company, St. Paul, Minn., a corporation of Delaware

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This invention relates to the reproduction of graphic originals, such as printed or typewritten correspondence, sketches, drawings and the like, by thermographic copying methods involving brief irradiation of the original with high intensity radiation, and formation of a visible reproduction of the resulting heat-image on a heat-sensitive copy-paper in heat-conductive pressure-contact therewith. The invention has particular reference to novel heat-sensitive copy-paper, in the preferred examples of which the sensitizing materials include phosphomolybdate or equivalent complex salts.

The preferred sensitizing materials employed in making the heat-sensitive copy-papers of this invention are water-soluble, and can therefore be applied to paper economically and safely in the form of aqueous solutions. However the reactants may also be dispersed in non-aqueous volatile liquid vehicles, preferably together with suitable soluble film-forming binders, and formed into visibly heat-sensitive films or coatings.

The preferred copy-sheets of this invention are based on complex phosphomolybdate salts and are white or very pale blue-green in appearance. They are stable at normal room and storage temperatures, under wide ranges of humidity, and when illuminated. When heated briefly to temperatures of the order of 60–150° C., e.g. by momentary contact with a heated metal bar, the copy-sheet rapidly converts to a deep blue color. The sheet produces clear and high-contrast reproductions of typewritten or other graphic originals in the thermographic copying process hereinabove identified. The areas corresponding to the radiation-absorptive printed areas of the original are converted to a dense blue; the background areas remain essentially unchanged. The sheet is sufficiently transmissive of infra-red radiation to permit "front-printing," in which the radiation reaches the printed surface of the original through the copy-sheet, with thermographic copying apparatus employing incandescent filament sources of radiation. Colored copy-sheets which when heated convert to contrasting colors or are otherwise visibly changed, or which differ in other respects from the preferred construction, may also be produced in accordance with the principles of the invention; but the normally white sheet producing a deep blue image is preferred.

In the drawing, Figure 1 represents a heat-sensitive copy-sheet **12** in front-print position over a graphic original **10** having radiation absorptive image areas **11**, the composite being irradiated from a source of radiation **14** to produce colored image areas **13** in the heat-sensitive copy-sheet. Figure 2 is a flow-sheet indicating the steps involved in producing a typical heat-sensitive copy-sheet in accordance with the principles of the invention.

The invention will now be further described in terms of specific illustrative but non-limitative examples in which all proportions are in parts by weight unless otherwise specified.

Example 1

Water	1000
Ammonium molybdate	40
Disodium acid phosphate	80
Magnesium chloride	280
Thiourea	80
Ascorbic acid	2.5
Sodium acetate	2.5

The reactants are dissolved in the water in the order named. Solution of the magnesium chloride results in the formation of a voluminous white precipitate, which is removed by filtration before adding the remaining components. The resulting solution is found to be unstable, becoming dark blue in color when allowed to stand at room temperature for 4–8 hours. It is therefore compounded and applied as rapidly as possible. Strips of thin translucent paper (map overlay tracing paper) are dip-coated with the solution and then dried rapidly in an air blast at not higher than 100° F. The resulting sheet is white or very faint blue in appearance, stable at normal room conditions, and converted to dark blue by brief contact with a metal bar at 100–120° C. The sheet is capable of providing a reproduction, by the thermographic copying process, of originals typewritten on letterhead bond paper.

Substitution of ammonium vanadate for ammonium molybdate in the formula of Example 1 provides a copy-sheet which requires somewhat more extensive heating for conversion to the colored form.

Example 2

Water	50
Ammonium molybdate	4
Na_2HPO_4	1
$MgCl_2 \cdot 6H_2O$	12
Sodium citrate	1.5
Ascorbic acid	0.25

The reactants are dissolved in the water in the order named. The final yellowish solution is slightly cloudy but remains visibly unchanged on standing over night at room temperature. The solution is applied to map overlay tracing paper in a number of successive very light coats by means of a transfer roll, with intermediate drying. The resulting copy-sheet produces clear high-contrast reproductions of typed originals by thermographic copying methods, the image areas appearing as a very deep blue on a substantially white background.

The application of a very thin opacifying coat, e.g. of a smooth dispersion of titanium dioxide pigment in a solution of a polymeric resin binder in a volatile organic solvent, increases the opacity of the sheet and results in increased contrast between image and background areas in the finished reproduction. Thin surface coatings of this or other unpigmented transparent resinous or binder material are similarly applicable as protective coatings where desired.

The slight cloudiness of the sensitizing solution may be overcome by reducing the amounts of ammonium molybdate and sodium acid phosphate by one-half, but the image density is also reduced. Increasing the concentration of reactants, e.g. to double the quantities shown, produces still more deeply but somewhat irregularly colored image areas in the copy; at these concentrations the solution is less stable, and a precipitate is formed.

Substitution of sodium thiosulfate for ascorbic acid in the foregoing formula produces a copy-sheet which converts from white to a weak dull brown at heated areas.

Example 3

Water	1000
$(NH_4)_6Mo_7O_{24}\cdot 4H_2O$	40
Na_2HPO_4	10
$MgCl_2\cdot 6H_2O$	240
NaCl (may be omitted)	40
Thiourea	80
Sodium citrate	20
Ascorbic acid	5

The components are combined as in the preceding examples, and applied to 27 lb. opaque greaseproof "Thilmany No. 908" paper, to provide a heat-sensitive copy-paper useful in the thermographic reproduction of graphic originals. The initially white sheet becomes a faint pink on prolonged exposure to sunlight without detracting from its ability to be rapidly converted to a deep blue on brief heating at 100–120° C.

Example 4

Water	50
Ammonium molybdate	2
$Na_2SiO_3\cdot 9H_2O$	1
Malic acid	1
Thiourea	2
$MgCl_2\cdot 6H_2O$	12

Copy-paper prepared with this solution produces a blue image with a light blue background. Stability of the sheet under room and storage conditions is improved by addition of small amounts of sodium citrate to the solution.

Example 5

Water	50
Ammonium molybdate	2
$Na_2HAsO_4\cdot 7H_2O$	1
$MgCl_2\cdot 6H_2O$	12
Sodium citrate	1
Ascorbic acid	0.25

The first two reactants are dissolved in the water at 180° F. The solution is then cooled to room temperature and the remaining ingredients are added and dissolved. Paper is dip-coated in the solution, dried, and tested as a heat-sensitive copy-sheet. The initially white sheet forms blue image areas on heating in the thermographic copy process.

Example 6

Tungstic acid, $WO_3\cdot 8H_2O$, 8 grams is dissolved in 200 ml. of water made slightly alkaline with sodium hydroxide and held at 80° C. The solution is brought to a pH of 6 with hydrochloric acid. There is then added 2 grams of disodium hydrogen phosphate and 48 grams of magnesium chloride, and the solution is cooled to room temperature. To a 50 ml. portion there is added 3 grams of sodium thiosulfate and 0.25 gram sodium citrate.

The solution is quickly applied to paper and dried, producing a normally stable copy-sheet which converts rapidly from a white to a blue appearance on heating to 100–120° C. and produces useful copy by thermographic copying procedures.

Substitution of ascorbic acid for sodium thiosulfate in this formula causes rapid conversion to a blue solution.

Molybdic oxide may similarly be dissolved by means of sodium hydroxide and the product used in place of the ammonium molybdate of Examples 1–5 or the sodium tungstate of Example 6.

Example 7

Sodium vanadate, $NaVO_3$, two parts, is dissolved in 50 parts of water with addition of sodium hydroxide and the solution brought to pH 6 with HCl as in the preceding example. The solution is reddish yellow. There is added one part of disodium acid phosphate and 12 parts of magnesium chloride. The solution is converted to an orange solution. Three parts of sodium thiosulfate is

then added, and the solution applied to paper and dried, producing a yellowish copy-paper which converts to blue at heated image areas in the thermographic copying procedure. Small amounts of sodium citrate may be included to improve stability.

Example 8

An aqueous solution of ammonium molybdate, disodium acid phosphate and magnesium chloride in the proportions shown in Example 3 is prepared and a portion is evaporated to dryness at room temperature. The solid residue is added to a solution of ethyl cellulose in acetone, and the mixture milled in a ball mill until smooth. Ascorbic acid in solution in alcohol is then added in the approximate proportions employed in Example 3, and the mixture is coated on paper and dried at room temperature. The sheet is heat-sensitive, providing useful reproductions of graphic originals by the thermographic copying process. The sheet is highly stable both under normal room conditions and at high humidities.

Another portion of the liquid mixture is spread on a smooth metal panel, permitted to dry, and then stripped from the metal surface to provide a self-sustaining heat-sensitive film product. The proportions of ethyl cellulose and heat-sensitive reactants are selected to provide a strong flexible film with adequate image-forming properties.

Water-soluble binder materials are similarly applicable. Thus, carboxymethyl cellulose, methyl cellulose, polyvinyl pyrrolidone and similar water-soluble film-forming materials are found useful in thickening aqueous solutions of these several reactant systems, to avoid displacement when applied to paper carrier webs at increased coating thicknesses, and in forming self-supporting heat-sensitive films.

Example 9

Ammonium molybdate is dissolved in water. With the solution boiling gently, aluminum chloride is cautiously added until a slight cloudiness begins to appear. The solution is then cooled by placing in an ice bath, whereupon a white crystalline precipitate is formed which is recovered. The precipitate is washed with ice-water and redissolved in warm water. To the solution are then added zinc chloride, sodium citrate, and ascorbic acid in the approximate proportions indicated in the previous examples, and the solution is applied to paper and dried. There is provided a heat-sensitive copy-paper which converts from white to dark blue in the thermographic copying process and when briefly contacted with a metal test bar heated to 100–120° C.

The initial precipitation may alternatively be accomplished by substituting potassium alum

$$(K_2SO_4\cdot Al_2(SO_4)_3\cdot 24H_2O)$$

for the aluminum chloride.

Example 10

Results analogous to those of Example 9 are obtained by adding directly, to 200 parts of water, 16 parts of ammonium molybdate, 20 parts of aluminum chloride, 4 parts of sodium citrate and one part of ascorbic acid. The reagents are added and dissolved in the order named while maintaining the solution at 140° F. Paper dipped in the solution and dried at room temperature produces a blue-green image under thermographic copying conditions. The sensitive sheet does not discolor nor lose sensitivity on prolonged storage or under accelerated test conditions of 50° C. and high humidity.

Example 11

The precipitate formed by cooling a hot solution of 2 parts of ammonium molybdate and one part of chrome alum is dissolved in warm water. Small amounts of ascorbic acid, malic acid, and zinc chloride are added. Paper is impregnated with the solution and dried, forming

a heat-sensitive copy-sheet which on heating produces a blue-green image.

Example 12

Cautious addition of ferric ammonium sulfate solution to warm ammonium molybdate solution produces a yellowish precipitate which redissolves on continued stirring. Cooling of the solution then produces a white precipitate, which is recovered, washed, and re-dissolved at 42° C. Small amounts of ascorbic acid and aluminum chloride are added and the solution applied to paper and dried, producing a heat-sensitive copy-sheet. The storage stability of the sheet is improved by addition of sodium citrate.

Example 13

To 50 parts of hot water there is added 6 parts of ammonium molybdate followed by 2 parts of cobalt chloride ($CoCl_2 \cdot 6H_2O$). A reaction occurs, forming a reddish purple semi-coloidal dispersion. To this is added 8 parts of potassium persulfate. A greenish solution results, which is cooled in an ice bath. The greenish crystalline precipitate formed is recovered on a filter, lightly rinsed with ice-water, and redissolved in 50 parts of warm water. One part of ascorbic acid is added, and the solution used to saturate paper which when dry is found to be useful as a heat-sensitive copy-paper, forming blue-black heated image areas on a light blue-green background.

Analogous results are obtained by first combining the cobalt chloride and potassium persulfate, then adding the ammonium molybdate, and proceeding as indicated.

Example 14

The formula and procedure of Example 13 is duplicated with the exception that manganese chloride ($MnCl_2 \cdot 4H_2O$) is substituted in equal weight for the cobalt chloride. An equally effective heat-sensitive copy-paper is obtained.

The heat required to cause image formation in the copy-sheets of Examples 13 and 14 may be further reduced by adding small amounts of magnesium chloride to the solution used for saturating or coating the paper. Such addition is particularly helpful where more dilute treating solutions are used.

Example 15

To a colorless solution of four parts of ammonium molybdate in water there is added a faintly pink solution of one part of manganese sulfate ($MnSO_4 \cdot H_2O$) in water, forming a reddish-yellow solution of reaction product from which is obtained a yellowish residue on evaporation in glass at elevated temperatures. When the solution is applied to paper or to aluminized paper or aluminum foil and dried at room temperature, the resulting sheet changes to a dark color on heating but requires excessive time and temperature of heating for effective use as a heat-sensitive copy-sheet. Heat-sensitivity is improved by the addition to the coating solution of small amounts of starch or thiourea.

When combined in aqueous solution under the conditions indicated, the molybdate and phosphate compounds of Example 1 react to form a heteropoly complex phosphomolybdate anion. Analogous reactions occur with the molybdate and silicate of Example 4, the molybdate and arsenate of Example 5, the tungstate and phosphate of Example 6, and the vanadate and phosphate of Example 7. Aluminum, chromium, iron, cobalt and manganese likewise form heteropoly complex anions with molybdenum and the like, as indicated in Examples 9–15. Similarly antimony, germanium, boron, copper, tellurium, titanium, selenium, zirconium, thorium and the like form oxygenated heteropoly complex anions with molybdenum, tungsten or vanadium. In these complex compounds the phosphorus or the like provides a central atom within an enclosing structure of molybdenum, tungsten or vanadium atoms and associated oxygen atoms. The availability of the central atom is thereby reduced; for example, magnesium chloride does not react with the stable colorless phosphomolybdate complex, whereas magnesium chloride and sodium acid phosphate in aqueous solution react readily, with precipitation of an insoluble magnesium phosphate. The anion is also difficultly reducible; but acidification of the heteropoly coplex results in polymerization and the resulting onion is then found to be easily convertible to an intensely colored modification by reaction with a mild reducing agent.

Each of the several elements which provide the central atom or atoms within the enclosing oxygenated structure of the heteropoly complex anion in the compositions and heat-sensitive copy-sheets of the foregoing examples, i.e. elements such as phosphorus, silicon, arsenic, aluminum, manganese, and various others, may be shown to respond to the following conditions:

a. The element in its ionic form has a positive valence of at least two.

b. The element has an ionic radius not less than about 0.20 Angstrom unit and not more than about 0.95 Angstrom unit, as calculated from crystal structure data.

c. The ion is capable of adding doubly charged negative oxygen atoms to its coordination sphere in neutral or acid solution, i.e., is capable of showing acidic character.

In addition, the preferred elements in low concentration are non-toxic by absorption or inhalation.

Magnesium chloride is readily hydrolyzed, at the temperatures involved in thermographic copying as herein described, to form hydrochloric acid and substantially water-insoluble magnesium hydroxide. Other equivalent water-soluble hydrolyzable salts of strong acids, effective in the copy-sheet compositions of this invention, include aluminum chloride, calcium chloride, cadmium chloride, lithium chloride, magnesium bromide, magnesium nitrate, magnesium sulfate, manganese chloride, manganese sulfate, nickel chloride, strontium chloride, zinc chloride, and zinc sulfate. On the other hand, barium chloride does not hydrolyze, the salt-forming reaction being dominant and barium hydroxide being highly water-soluble at the copying temperature. The same is true of the sodium and potassium salts of strong acids. These salts are ineffective for the purposes of the invention. Again, salts of metals such as mercury, tin and antimony, which in aqueous solution provide easily oxidizable metal cations, cannot effectively be introduced in the sensitizing solution without immediate inter-reaction and are therefore to be avoided for the present purposes. Strong-acid salts of metals such as iron, chromium, and cobalt, in which the metal ion is not readily oxidizable, have been used, but are themselves strongly colored and tend to reduce the contrast obtainable in the resulting copy, and hence are less desirable than the colorless or lightly colored salts. Calcium nitrate has been usefully substituted for magnesium chloride in these formulations but the resulting sheet is somewhat less stable on storage and this type of compound, like the strongly colored salts, is not ordinarily preferred.

Stability of the copy-sheet involves the ability of the sheet to remain rapidly visibly reactive on prolonged storage. The sheet must not discolor or darken to any appreciable extent and the color-forming reaction must not occur prematurely. Many of the compositions here described produce copy-sheets having adequate stability for many purposes even in the absence of specific stabilizer materials; however it is generally found desirable to further stabilize the compositions by the addition of a stabilizer, such for example as a water-soluble salt of a weak acid having an ionization constant of about 10^{-3} to 10^{-7} or even somewhat lower. Preferred examples include ammonium or alkali metal citrates, tartrates, acetates, formates, lactates, benzoates, phthalates and malates. Carbonates and bicarbonates are less effective but still useful.

In general, water-soluble reducing agents which exhibit a mild reducing action in acid solution are useful in these heat-sensitive copy-sheets. Ascorbic acid is a preferred material in many of these compositions. With ascorbic acid as the sole reducing agent, the composition will ordinarily require increased amounts of stabilizer. Ascorbic acid is also expensive. On the other hand, thiourea is relatively inexpensive and sheets made with this material are stable with much lower amounts of stabilizer; but higher activation temperatures are then required. A combination of thiourea and ascorbic acid, as provided in a number of the examples, is found to be surprisingly stable even under accelerated test storage conditions, and to produce excellent images at readily available temperatures. Other mild reducing agents which have been found useful, either alone or in combination, as components of the heat-sensitive copy-sheets of this invention include itaconic acid, malic acid, Elon (para-aminophenolsulfate), and tartaric acid.

In some cases, extremely mild reducing agents are found to produce only a slight visible change on heating of the copy-sheet. Sodium thiosulfate in the modified formula of Example 2 provides one such formula. On the other hand, strong reducing agents, and particularly those which are at the same time strongly acidic, such for example as stannous chloride, have been found to cause immediate conversion of the phosphomolybdate or equivalent complex to the colored modification.

Although the mechanism involved has not been fully explicated, it is believed that the brief heating of the copy-sheet during the thermographic process hereinbefore described results in the following series of reactions. On heating, acid is first liberated, by hydrolysis of magnesium chloride in the presence of liberated water or water vapor. The presence of acid causes rearrangement of the phosphomolybdate or equivalent complex from the initially stable form to a readily reducible modification. In some instances the acid also presumably imparts additional activity to the reducing agent or agents. In any event, at the temperatures involved, the latter material then reacts with the readily reducible phosphomolybdate complex, reducing it to a strongly colored product and thereby causing a visible change at the heated areas. Whatever the explanation, and regardless of theory, copy-sheets prepared as hereinbefore indicated are found to be stable under normal handling, storage, and exposure conditions, to be distinctly and permanently visibly changed when tested by pressing momentarily against a metal test bar heated to a temperature within the range of about 60–150° C., and to be capable of effectively copying typewritten and other graphic originals by means of thermographic copying procedures as hereinbefore outlined.

What is claimed is as follows:

1. A heat-sensitive copy-sheet suitable for the thermographic reproduction of graphic originals, capable of permanently converting to a visibly distinct form on being momentarily pressed against a metal test bar at a temperature within the range of about 60–150° C., and including a visibly heat-sensitive layer comprising: a water-soluble compound of a cation and a difficultly reducible heteropoly complex oxygenated anion having a central atom within an enclosing structure of atoms selected from the class consisting of molybdenum, tungsten and vanadium, and mixtures thereof; a water-soluble hydrolyzable salt selected from the class consisting of aluminum chloride, calcium chloride, cadmium chloride, lithium chloride, magnesium bromide, magnesium chloride, magnesium nitrate, magnesium sulfate, manganese chloride, manganese sulfate, nickel chloride, strontium chloride, zinc chloride, and zinc sulfate; and a water-soluble reducing agent having a mild reducing action in acid solution.

2. A heat-sensitive copy-sheet suitable for the thermographic reproduction of graphic originals, stable under normal room, storage and handling conditions, and capable of permanently converting to a visibly distinct form on being momentarily pressed against a metal test bar at a temperature within the range of about 60–150° C., and including a stabilized visibly heat-sensitive layer consisting essentially of: a water-soluble compound of a cation and a difficultly reducible heteropoly complex oxygenated anion having a central atom within an enclosing structure of atoms selected from the class consisting of molybdenum, tungsten and vanadium, and mixtures thereof; a water-soluble hydrolyzable salt selected from the class consisting of aluminum chloride, calcium chloride, cadmium chloride, lithium chloride, magnesium bromide, magnesium chloride, magnesium nitrate, magnesium sulfate, manganese chloride, manganese sulfate, nickel chloride, strontium chloride, zinc chloride, and zinc sulfate; a water-soluble reducing agent having a mild reducing action in acid solution; and, as a stabilizer material, a water-soluble salt of a weak organic acid having an ionization constant not greater than about 10^{-3}.

3. A heat-sensitive copy-paper suitable for the thermographic reproduction of graphic originals, stable under normal room, storage and handling conditions, and capable of permanently converting to a visibly distinct form on being momentarily pressed against a metal test bar at a temperature within the range of about 60–150° C., comprising a paper support member and a stabilized visibly heat-sensitive layer consisting essentially of: a water-soluble compound of a cation and a difficultly reducible heteropoly complex oxygenated anion having a central atom within an enclosing structure of atoms selected from the class consisting of molybdenum, tungsten and vanadium, and mixtures thereof; a water-soluble hydrolyzable salt selected from the class consisting of aluminum chloride, calcium chloride, cadmium chloride, lithium chloride, magnesium bromide, magnesium chloride, magnesium nitrate, magnesium sulfate, manganese chloride, manganese sulfate, nickel chloride, strontium chloride, zinc chloride, and zinc sulfate; a water-soluble reducing agent having a mild reducing action in acid solution; and, as a stabilizer material, a water-soluble salt of a weak organic acid having an ionization constant within the range of about 10^{-3} to 10^{-7}.

4. The copy-paper of claim 3 in which the paper support member is porous and is at least partially impregnated with the intermixed components of the heat-sensitive layer.

5. The copy-paper of claim 3 in which the paper support member is coated with the heat-sensitive layer, the latter including a film-forming binder.

6. A heat-sensitive copy-paper as defined in claim 3 and including a protective heat-stable continuous film-like surface coating.

7. A stable heat-sensitive copy-paper suitable for the thermographic reproduction of black-on-white graphic originals as blue-on-white copies, capable of permanently converting from a white to an intense blue form on being momentarily pressed against a metal test bar at a temperature within the range of about 60–150° C., comprising a thin flexible paper support member carrying a visibly heat-sensitive layer consisting essentially of water-soluble difficulty reducible phosphomolybdate complex heteropoly compound, magnesium chloride, ascorbic acid, and sodium citrate.

8. A heat-sensitive copy-sheet suitable for the thermographic reproduction of graphic originals, stable under normal room, storage and handling conditions, and capable of permanently converting to a visibly distinct form on being momentarily pressed against a metal test bar at a temperature within the range of about 60–150° C., comprising a paper support member and a thin, stable, visibly heat-sensitive coating of a film-forming water-insoluble polymeric organic binder containing, uniformly dispersed therein, components comprising: a water-soluble

compound of a cation and a difficultly reducible heteropoly complex oxygenated anion having a central atom within an enclosing structure of atoms selected from the class consisting of molybedenum, tungsten and vanadium, and mixtures thereof; a water-soluble hydrolyzable salt selected from the class consisting of aluminum chloride, calcium chloride, cadmium chloride, lithium chloride, magnesium bromide, magnesium chloride, magnesium nitrate, magnesium sulfate, manganese chloride, manganese chloride, manganese sulfate, nickel chloride, strontium chloride, zinc chloride, and zinc sulfate; and a water-soluble reducing agent having a mild reducing action in acid solution.

9. A stable heat-sensitive copy-paper suitable for the thermographic reproduction of black-on-white graphic originals as blue-on-white copies, capable of permanently converting from a white to an intense blue form on being momentarily pressed against a metal test bar at a temperature within the range of about 60–150° C., comprising a thin flexible paper support member carrying a visibly heat-sensitive layer consisting essentially of: a water-soluble difficultly reducible aluminomolybdate complex heteropoly compound; aluminum chloride; a water-soluble reducing agent having a mild reducing action in acid solution; and, as a stabilizer material, a water-soluble salt of a weak organic acid having an ionization constant within the range of about 10^{-3} to 10^{-7}.

10. The method of making a heat-sensitive copy-sheet suitable for the thermographic reproduction of graphic originals and capable of permanently converting to a visibly distinct form on being momentarily pressed against a metal test bar at a temperature within the range of about 60–150° C., comprising: coating on a receptive thin flexible support web a liquid composition comprising a volatile liquid vehicle, a water-soluble compound of a cation and a difficultly reducible heteropoly complex anion having a central atom within an enclosing structure of atoms selected from the class consisting of molybdenum, tungsten and vanadium, and mixtures thereof, a water-soluble hydrolyzable salt selected from the class consisting of aluminum chloride, calcium chloride, cadmium chloride, lithium chloride, magnesium bromide, magnesium chloride, magnesium nitrate, magnesium sulfate, manganese chloride, manganese sulfate, nickel chloride, strontium chloride, zinc chloride, and zinc sulfate, and a water-soluble reducing agent having a mild reducing action in acid solution; and drying said coating while avoiding interreaction of said composition.

11. A stable heat-sensitive copy-paper suitable for the thermographic reproduction of black-on-white graphic originals as blue-on-white copies, capable of permanently converting from a white to an intense blue form on being momentarily pressed against a metal test bar at a temperature within the range of about 60–150° C., comprising a thin flexible paper support member carrying a visibly heat-sensitive layer consisting essentially of water-soluble difficultly reducible phosphomolybdate complex heteropoly compound, magnesium chloride, a water-soluble reducing agent having a mild reducing action in acid solution, and, as a stabilizer material, a water-soluble salt of a weak organic acid having an ionization constant within the range of about 10^{-3} to 10^{-7}.

12. A heat-sensitive copy-sheet suitable for the thermographic reproduction of graphic originals, and capable of permanently converting to a visibly distinct form on being momentarily pressed against a metal test bar at a temperature within the range of about 60–150° C., said copy-sheet including a visibly heat-sensitive layer comprising: a water-soluble compound of a cation and a difficultly reducible heteropoly complex oxygenated anion having a central atom within an enclosing structure of atoms selected from the class consisting of molybdenum, tungsten and vanadium, and mixtures thereof; magnesium chloride; water-soluble reducing agent having a mild reducing action in acid solution; and, as a stabilizer material, a water-soluble salt of a weak organic acid having an ionization constant within the range of about 10^{-3} to 10^{-7}.

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