

July 26, 1966

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DUPLICATING METHOD
Filed Nov. 23, 1959

3,262,386

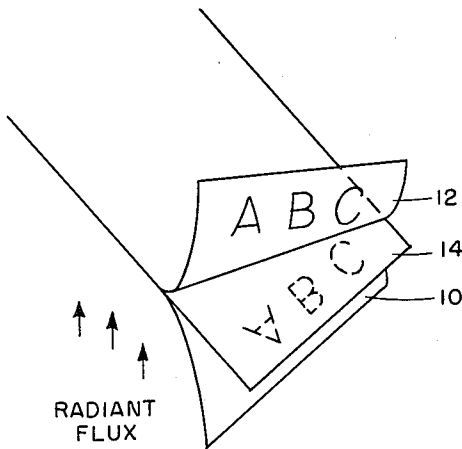


Fig. 1

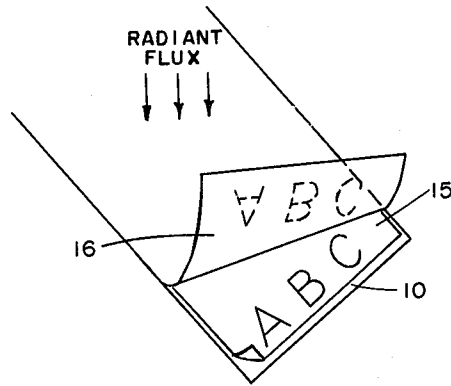


Fig. 2

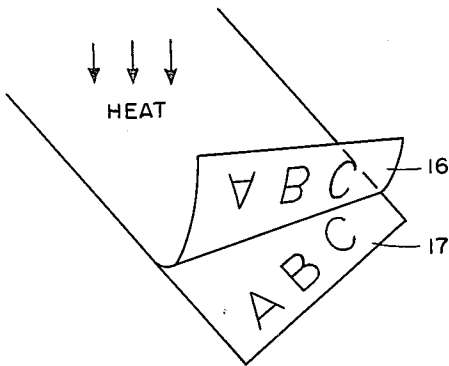


Fig. 3

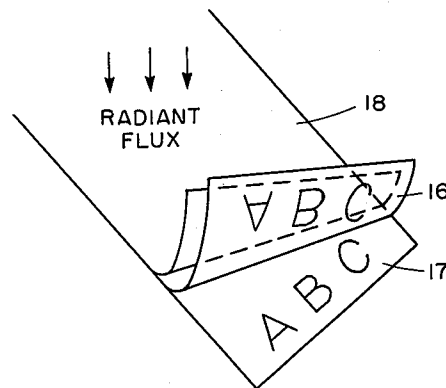


Fig. 4

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DUPLICATING METHOD

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Filed Nov. 23, 1959, Ser. No. 854,909

7 Claims. (Cl. 101—149.4)

This invention relates to a system for producing copy from an original or from a master and to articles of manufacture for use in the system. More particularly this invention relates to a new and improved thermographic system for reproducing copy.

There are available a number of systems for making copies directly from an original, some of which are based upon the fact that chemical reactions are sensitized by heat which is absorbed and transmitted by indicia on an original. Most of the systems for producing copy now available which are reasonably rapid are not capable of producing a permanent copy. Thus many of the copy systems are suitable for making reproductions which are adequate for a limited period of time but which are affected either by light or heat or both whereby the copy becomes eligible.

It would be desirable to have available a method by which original documents, half-tone prints and the like, usually in black and white, could be copied accurately and rapidly to give a permanent record or copy. The method and article of manufacture of this invention provide such a means for copying.

It is therefore an object of this invention to provide a method whereby many types of documents, including half-tone prints, may be copied accurately and rapidly. It is another object to provide methods of the above-identified character which are capable of making reproductions or copies exhibiting good copy quality and which are not subject to the deleterious effects of light and heat and hence are available as permanent records. It is yet another object of this invention to provide a method and articles of manufacture of the character described which permit making copies in a variety of colors. It is a further object to provide a method and articles of manufacture for making copies of originals which may be relatively dense or thick and for making copies of originals which may be printed on both sides.

It is a further object of this invention to provide a copying medium which is capable of being fixed, i.e., rendered incapable of producing additional copies on the same sheet after it has been treated by a fixing process. It is still another object of this invention to produce from documents and other original material a copy which will survive and remain legible after prolonged immersion in water and after continued handling, folding, soiling and abrasion. It is still yet another object of this invention to provide a means of making copies from a master which may be made directly rather than made from an original. These and other objects will become apparent in the description which follows.

The method of reproducing a copy from an original or from a master copy in accordance with this invention may be described as characterized by the step of depositing on a receptor or copy sheet a chelating compound which undergoes sublimation at a temperature between about 80 and 200° C. in areas corresponding to the indicia to be copied, whereby the chelating compound in these areas is available for reaction with metallic ions to form a water insoluble chromophoric complex to give a colored reproduction of the indicia on a copy sheet containing the metallic ions.

The method of this invention may be further characterized as being of either the direct or of the reflex type. In

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the direct method, the chelating compound is sublimed directly onto the copy sheet; in the reflex method the chelating compound is first sublimed onto a master tissue in areas corresponding to the indicia to be copied and then in a second step, it is transmitted from the master tissue to the copy sheet which contains the metallic ions. A master tissue may also be formed, as described later, by imprinting the chelating compound directly on the tissue and then causing the chelating compound to react with the metallic ions in the copy sheet under the conditions specified.

The operation of the method of this invention is based upon the sublimation of a first reactant present on a transfer sheet to a copy sheet either directly or in a two-stage process, the latter involving the production first of a master receptor tissue. The sublimed reactant may react immediately or be caused to react later with a second reactant in or on the copy sheet. The reaction which takes place between the sublimed reactant and the reactant in the copy sheet should, of course, give rise to the production of a chromophoric complex, i.e., one capable of producing a color. Moreover, the chromophoric complex should be one which is substantially insoluble in water, thus making the final copy impervious to moisture. It should also be insensitive to light and to heat to give a final permanent copy.

The amount of reactant which is sublimed from the transfer sheet or from the master receptor tissue and thus transferred to the copy sheet will depend upon the temperature reached at the point of transfer and hence the system is capable of reproducing continuous tones.

The reactant which is to be sublimed and transferred to the copy sheet for reaction with the metallic ions contained thereon may be defined as a chelating compound capable of undergoing sublimation without appreciable decomposition in a temperature range from about 80 to 200° C. Moreover, it should be a material which reacts with the metallic ions to give a water-insoluble, light and heat insensitive colored reaction product which is thus responsible for producing the colored copy in the copy sheet.

I have found that dithioamide, $C_2S_2(NH_2)_2$ (commonly known as rubeanic acid) is ideally suited for the chelating compound which is to be vaporized or sublimed from the transfer sheet or from the master receptor tissue to the copy sheet for subsequent reaction.

Dithioamide sublimes readily at a temperature of about 150° C. without decomposition and hence may be transferred to the copy sheet by the application of heat. Moreover dithioamide forms a stable complex with a number of metallic ions among which may be listed nickel, cobalt, copper, lead, mercury, silver and various other so-called transition metals in the periodic table. Mixtures of these various metallic ions may be used to achieve desired colors and sensitivities. Of these metallic ions, I have found that nickelous ions are particularly suited for the practice of this invention and that the copy which results from their use is a pleasing blue, the color depending to some extent upon the nature of the substrate, i.e., copy sheet, as well as on the concentration of nickelous ions.

It is preferable that the metallic compound in the copy sheet available for reaction is present in a hydrated form. It is believed that the presence of the water of hydration in the reactant contributes materially to the reaction in the role of a "developing medium" within the copy sheet. It is also preferable to have a relatively high moisture content, about 5% by paper weight, in the copy sheet when the copy is made; this moisture content can easily be maintained by known moisture-conditioning techniques.

However, in order to develop adequately the image formed by the reaction of the chelating compound and

the metallic ion it may be necessary to provide an additional developing medium for the reaction. Such developing medium may include water (part of which may be furnished by the hydrated reactant in the copy sheet and the moisture adsorbed in the copy sheet) condensed steam, or an ionizing medium such as molten urea or a molten salt hydrate. I have found that where dithioamide is used as the chelating compound, urea is particularly well adapted to this use and that it can be provided in the copying method of this invention either by incorporating it in the copy paper or in the transfer sheet containing the dithioamide. It appears that if the urea is initially placed in the transfer sheet some of it is transferred onto the copy sheet along with the dithioamide. If, on the other hand, the urea is incorporated into the copy sheet, it is available as a reaction medium when required, where the urea acts as a flux for the reaction between the dithioamide and the metallic ion of the salt present on the copy sheet. It is also possible that in acting as a flux the urea enters into the reaction that produces copy.

In order to better understand the mechanism by which the reproduction or copying system of this invention operates, reference may be made to the drawings in which:

FIG. 1 illustrates a direct method of reproduction;

FIGS. 2 and 3 illustrate the two steps in the offset or reflex method; and

FIG. 4 illustrates a variation in the offset or reflex method.

With reference to FIG. 1, in which a direct method of reproduction is illustrated, there is shown the original sheet 10 on which the indicia to be copied are located, the copy sheet 12 containing the metallic ions, and the transfer sheet 14 which is impregnated or treated with the chelating compound. In the method illustrated in FIG. 1 the reaction medium such as urea may be present either in the transfer sheet 14 or in the copy sheet 12. In this direct method it is convenient to interpose the transfer sheet 14 between the original 10 and the copy sheet 12 and then to expose the assembly while the surfaces of the sheets are in direct contact to radiant flux which is incident on the original 10 as shown in FIG. 1. In this arrangement the radiant flux will strike the side of the original on which the indicia to be copied are located. Where indicia such as indicated by dotted lines in FIG. 1 are located on the original heat will be produced, transmitted through the original to the tissue thus causing the dithioamide or other chelating compound in those portions or areas of the tissue which are heated to sublime and be transferred to the copy sheet. The dithioamide then reacts with the metallic ions, for example nickel, in the copy sheet to produce a chromaphoric complex and give a colored image as shown in solid lines in FIG. 1 on the copy sheet 12 which corresponds to the indicia present on the original 10.

The transfer sheet treated with the chelating compound may be used a number of times. If a noticeable change of color (from orange to yellow in the case of dithioamide) takes place, the transfer sheet may be heated to redistribute the chelating compound within the transfer sheet. This may be done by covering it with a sheet of black or dark gray paper and exposing the cover sheet to radiant flux.

The direct method illustrated in FIG. 1 is especially suitable for copying originals on thin paper such as carbon copies on onionskin, drawings on drafting paper, and the like. When the original is on heavy paper a certain amount of fuzziness may develop in the final copy due to some lateral spreading of the thermal pattern and to the sideways diffusion of vapor of the dithioamide. A further limitation of this direct system is that it provides only single copies and therefore the procedure must be repeated for each copy.

The method of reproduction of this invention is adaptable to a two-stage offset or reflex technique which is illustrated in FIGS. 2 and 3. In this second technique a master receptor sheet is made from which a number of copies may then be produced. The first step of the two-stage

or reflex process consists of interposing a transfer sheet 15 containing the chelating compound between the original 10 and a master receptor tissue 16. The assembly of sheets with the original indicia (solid lines) facing the transfer sheet 15 and with the surfaces in direct contact as illustrated in FIG. 2 is then exposed to an intense radiant flux as illustrated in FIG. 2. The exposure results in localized heating where indicia are located in the original and in these areas of localized heating the dithioamide is transferred to the master receptor tissue 16 in the areas corresponding to the original areas of the indicia and in direct proportion to the ability of the indicia of the original to absorb and transmit heat. The master receptor tissue 16 then has indicia (dotted lines) in the form of a reverse image in the chelating compound.

The second step then consists of using the master receptor tissue 16 in the production of copies on copy paper 17. This is conveniently done as illustrated in FIG. 3 by contacting the surface of the copy paper 17 and the master tissue 16 and exposing the resulting assembly to a source of heat to cause the chelating compound on the master receptor tissue to sublime onto the copy sheet and react thereon with the metallic ion. The source of heat may conveniently be a heated roller, platen, or the like.

An alternate way of using the master receptor sheet 17 is to form an assembly such as illustrated in FIG. 4 where the master receptor tissue 16 may be interposed between a copy sheet 17 and a sheet capable of absorbing radiant flux in the form of heat, such as a piece of black or gray paper 18. This assembly may then be exposed to radiant flux rather than to heat, thus making it possible to use the same equipment for the two methods illustrated in FIG. 1 and in FIGS. 2 and 3.

In the two-stage reflex method illustrated in FIGS. 2 through 4 all of the dithioamide will not be transferred from the master receptor tissue 16 to the copy sheet 17 in a single operation. This means that it is possible by the reflex method to make a number of duplicate copies from one master tissue.

The quality of the copy obtained by the offset or reflex technique of FIGS. 3 and 4 is sharper than that illustrated by the direct technique in FIG. 1. Moreover it has been found that the copy obtained in the offset or reflex technique compares very favorably in the quality of reproduction with present methods achieved through photographic techniques and does not, of course, require the steps of exposure, developing, printing, etc., required in photographic copying. Thus the process of this invention is capable of producing copies of a quality equivalent to photocopy and moreover possesses the inherent advantages of being a dry process which does not require any darkroom techniques.

Master receptor tissues may be prepared in yet another manner, that is by direct deposition of the chelating compound on the receptor tissue without the use of an original copy. For example, master sheets for the production of copies according to this invention as illustrated in the steps shown in FIGS. 3 and 4 may be made directly by placing a transfer sheet containing dithioamide or other chelating compound against the back face of a receiving or receptor sheet and marking on the top surface of a receptor sheet either directly or through another sheet. By this way offset masters corresponding to master tissue 16 of FIGS. 2 through 4 can be made for direct duplication as illustrated in FIGS. 3 and 4.

In the preparation of the transfer sheet to be used in the direct process (e.g., sheet 14 of FIG. 1), which is to contain the chelating compound, e.g., dithioamide with or without the developing medium, it has been found convenient to immerse the tissue used in making the transfer sheet in a solution of the chelating compound and then to remove the solvent by any known technique. Thus dithioamide for the direct process is conveniently introduced into a tissue in the form of a 2% solution in methyl ethyl ketone. The resulting treated tissue is then dried

by any known paper drying techniques to form the transfer sheet. The total residue of dithioamide in the sheet after drying preferably ranges from about 2 to 8% of the weight of the paper, however, this amount is not critical. These sheets require no precautions in handling or storing except that it is not desirable to expose them to temperatures above the sublimation temperature of the chelating compound. Thus in the case of dithioamide it would not be desirable to expose the transfer sheet to temperatures above about 125° C.

In the direct process it is desirable but not essential to place a developing medium on the transfer sheet along with the chelating agent. In the case of dithioamide, urea is the preferred developing medium and this may be conveniently put on the sheet after the dithioamide by running it through a water solution containing 30% urea, after which the sheet is dried.

The paper stock to be used for the transfer sheet in the direct process may be any good quality tissue, but a very porous sheet is desirable. A preferable type of tissue is one which has been formed from Manila rope fibers. This tissue is not only porous and capable of retaining a satisfactory amount of the chelating compound, but it is also strong and durable.

For the copy sheet in the direct process, the metallic ions may be introduced conveniently in the form of a water solution and the solution may be applied by any known technique such as by contacting the surface of the copy sheet stock with the solution or by using coating rods or other known coating techniques. In the case of nickelous ions, for example, it has been found convenient to coat the copy paper stock with a 10% concentration of a hydrated nickelous acetate. The resulting copying paper is then dried by any suitable drying technique known and is ready for use. The weight range of the metallic compound used to furnish the necessary metallic ions present in the sheet may vary over a fairly wide range, for example, from about 1 to 10% by weight. It is, however, preferred that the metallic compounds be present in the copy sheet in a concentration equivalent to about 3% by weight of the copy sheet. This figure will depend on the weight of the copy sheet and the manner in which the metallic salt is applied. As in the case of the tissue no precautions are required in the handling or storing of the copy paper, although, for best results, it is desirable to maintain a relatively high moisture content, for example about 5%.

Other metallic ions may, of course, also be used. For example, lead may be introduced as lead acetate or cobalt as cobalt chloride. Although the developing medium, such as urea, may be deposited on the copy sheet, it is preferred for the direct process to place it in the transfer sheet as described above. When the reaction medium is on the copy sheet, it may be present in an amount ranging from about 1.5 to 10% of the weight of the copy sheet.

It has been found that since only a portion of the chelating compound is sublimed from the transfer sheet in the direct process, it is possible to use this transfer sheet over again several times. There is some evidence of a change in color (for example, from orange to yellow in the case of dithioamide) and a visual examination can be employed to determine when the chelating compound in the tissue has been exhausted.

The reflex method involves three different types of sheets: a transfer sheet which contains the chelating compound, a master sheet which receives the sublimed chelating compound, and the copy sheet on which the final image is formed after transfer of the chelating compound from the master. In this method, as in the direct process, the copy sheet contains metallic ions which react with the chelating compound in the presence of a developing agent to form an insoluble chromophoric complex. In the reflex method, it is preferred to incorporate the developing

medium, such as urea, in the copy sheet rather than in the transfer sheet.

In the reflex method transfer sheet, the chelating compound is preferably applied in a resinous surface coating. A desirable coating mixture for dithioamide contains about 2% of the chelating compound and about 10% of ethyl cellulose dissolved in methyl ethyl ketone. This lacquer solution is coated on the transfer tissue with a wire-wound coating rod or any other known technique.

After being coated and dried, the sheet is left with a clear film containing the chelating compound. A desirable coating weight is from about 3 to 5 grams per square meter of paper of which 0.45 to 0.75 gram is the chelating compound. If the concentration of the chelating compound in the film is much greater than this, crystals tend to form as a "bloom" in the coating and this has an undesirable effect on the copy.

The reflex master sheet acts as a collector of the vaporized chelating compound; it must therefore remain relatively cool during the exposure step. In order to prevent the master sheet from being appreciably heated by thermal contact with the transfer sheet, a fine-grained inert material such as silica may be incorporated in the transfer sheet coating in order to give it a fine sandpaper-like texture. Particles of silica gel in the size range that will pass through a 140-mesh screen and be retained on a 200-mesh screen have been found adequate for this purpose. The amount of such suspended particles in the coating solution should not be greater than about 2% by weight of the solution.

The copy sheet for the reflex method is similar to that in the direct method except that it is desirable in this case to add a developing medium such as urea to the copy sheet. A sheet coated with a water solution containing 15% nickelous acetate and 20% urea proves satisfactory. The weight of solids coated on the copy sheet paper will vary from about 2% to 20% depending on the concentration in the coating solution, the absorptivity of the paper, the dwell time in the coating bath and the like; a pick-up of about 5% based on the weight of the paper is preferred. About equal weights of the metallic salt and developing medium are desired.

The most suitable paper stock for the transfer sheet in the reflex process has been found to be a very thin dense tissue. Thus a fine tissue known as Washington Linen sold by Peter Schweitzer Company which weighs only 4.5 pounds per ream (500 sheets, 22 x 35", basis) has been used with good success. The requirements for the master tissue are not critical, but a light porous sheet is preferred. A Manila rope tissue is excellent. For the copy sheet a fairly heavy absorbent stock is preferred similar to that used for the copy sheet of the direct process.

Since the copy produced in the copy sheet in the practice of this invention is in the form of a water-insoluble complex it is possible to fix the copy and to treat the copy sheet so that further exposure of it to chelating compound will not introduce additional marks or indicia in the copy sheet. For example, a convenient way is to wash the copy sheet in water thus removing the unreacted water-soluble metallic ions, leaving the water-insoluble indicia intact on the copy sheet. Thus, a permanent record is imparted to the copy sheet which cannot be altered and which cannot be destroyed over extended periods of storage through the deleterious effects of heat, light or moisture.

The total radiant energy required for the process of the operation of this invention is about the same for either the direct or reflex methods and is comparable with that for other known thermographic processes. A difficulty in some known thermographic methods results from the fact that the copy that is produced in the "reflex" relationship to the original is itself capable of absorbing radiation; thus, during the copying process, the darker parts of the copy tend to become abnormally dark and

spread out by a process that might be termed "autocatalysis" which results from absorption of radiant energy in the copy itself. The direct process of this invention is, of course, entirely free from the difficulty of autocatalysis because the radiant energy does not strike the copy directly. Even in the reflex process of this invention, autocatalysis presents no problem because no dark, radiation absorbing image is produced during the time that radiant energy is incident on the system.

The exposure to radiant flux in the copying process of this invention is a function of both intensity and duration and may be easily determined experimentally for the various types of originals to be copied. The chelating compound must, of course, be exposed to sufficient intensity of heat to sublime and to effect the required transfer of this material eventually to the copy sheet.

The process for duplicating according to this invention and the manner in which the transfer sheets and the copy paper are prepared are further described in the following examples which are meant to be illustrative and not limiting.

Example I

Copy paper was first prepared by drawing over the surface of a water solution containing 10% nickelous acetate by weight sheets of an uncalendered 50-pound sulfite pulp paper (ream, 22-inch x 35-inch, 1000-sheet basis). The sheets were left to dry in the atmosphere to remove essentially all of the water. The nickelous acetate was present in a hydrated form in the dry paper in an amount equivalent to 3% by weight of the paper.

The tissue suitable for the direct reproduction method (FIG. 1) was prepared by drawing a Manila rope fiber porous tissue through a 2% solution of dithioamide in methyl ethyl ketone. The tissue was then dried to remove the methyl ethyl ketone and it was found that the dithioamide pick-up was equivalent to 2.5% by weight of the paper weight. The treated tissue was then further treated with urea by drawing the dithioamide containing tissue sheets over the surface of a 30% water solution of urea. The sheet was again dried and the urea pick-up was found to be 90% by weight of the untreated sheet.

A sheet of light bond paper on which a text had been typewritten was used as the original. The original, tissue and copy sheet were arranged as in FIG. 1 with the unmarked or untyped side of the original contacting the tissue. The assembly was then passed through a machine designed to expose the printed side of the original to an intense light. The machine used was one sold by Minnesota Mining and Manufacturing Company under the trade name of Thermofax.

Subsequent to the exposure of the assembly to the intense light the sheets were separated and there appeared on the copy sheet indicia corresponding to the typed text on the original. The indicia were a deep, rather bright blue and the copy quality was rated as good.

Example II

Copy paper was prepared by drawing over the surface of a water solution containing 10% nickelous acetate and 20% urea sheets of the uncalendered paper used in Example I. The treated sheets were left to dry to remove essentially all of the water. The nickelous acetate was present in hydrated form in an amount equivalent to 3% by weight of the paper while the urea was present in an amount equivalent to 6%.

A tissue suitable for the offset or reflex method (FIG. 2) was prepared by rod coating a sheet of Washington Linen paper from the Peter Schweitzer Company (basis weight 4 lb. for 1 ream of 22-inch by 35-inch sheets) with a solution containing 2% of dithioamide, 10% of ethyl cellulose type N50 and 1.5% silica gel which passed a 150-mesh screen in methyl ethyl ketone. This tissue was dried to remove the methyl ethyl ketone and was then ready to be used in the preparation of a master

tissue. The weight of the deposited film was about 4 grams per square meter of paper.

To prepare the master tissue the original of Example I was assembled with the above coated transfer tissue and an untreated Manila rope tissue as illustrated in FIG. 2. That is, over the typed side of the original was first placed the treated tissue with the uncoated side facing the original and on top of this the untreated Manila rope tissue which was to become the master tissue. The assembly was then exposed to radiant energy from an incandescent lamp on a machine which was arranged to hold the transfer sheet in close contact with the original by means of vacuum and to permit the master tissue to remain in light contact with the transfer tissue. By this method the dithioamide from the transfer sheet was sublimed and deposited on the master tissue in areas corresponding to the indicia on the original. Thus there was produced a reverse image of the original on the master tissue. This master tissue was then available for making a number of duplicate copies on the copy paper prepared as indicated.

Copies were made by two different methods. The copy paper and the master were contacted in a manner so that the resulting copy would again be reversed to produce a replica of the original as in FIG. 3. The assembly along with a protective sheeting on the back of the copy paper was pressed between heated platens whereby a portion of the dithioamide in the master copy was sublimed for reaction with the nickelous acetate in the presence of the urea in the copy paper. Inasmuch as only a portion of the dithioamide was thus sublimed it was possible to use the master copy over a number of times, e.g., as many as 6 times.

The master copy was employed in another manner which comprised forming an assembly of the master tissue, the copy paper and a sheet of black paper over the master tissue. This assembly was then passed through the machine described above in such a manner that radiant flux struck the black paper. It was thus possible to use radiant flux rather than heat directly, inasmuch as the black paper served to convert the radiant flux to heat and thus to act in the manner of a heated platen.

In either case the final copy in the copy paper was a deep blue and the copy quality was excellent. That is, there appeared to visual inspection to be no lateral spreading of the indicia.

Example III

The sample copies prepared in Examples I and II were fixed by washing the copies with water in a photographic developing tray for a brief period, e.g., one to two minutes, thus dissolving out the excess nickelous acetate contained in the copy sheets. The copies were then dried. No visual change in copy quality or intensity could be noted in the indicia thereon. When attempts were made to make additional marks on these copies by the direct or by the reflex method they were unsuccessful. This indicates the advantage of the duplicating system of this invention in that it is possible to fix the indicia and to render the copy unalterable.

Example IV

Copy paper was prepared in the same manner as in Example I except that a 10% solution of cobaltous chloride was used instead of nickelous acetate. The process was repeated with a similar transfer sheet as used in the first example. A golden yellow copy was obtained which was however not considered to have sufficient contrast for ordinary duplicating applications.

The procedure was repeated with a coating solution for the copy sheet consisting of a mixture of 5% cobaltous chloride and 5% nickelous acetate. In this case a copy was obtained which had a pleasing gray color and which was highly legible.

Example V

A copy was made as in Example I except that the coating solution for the copy paper contained 10% of lead

acetate instead of nickelous acetate. The copy had a pleasing sepia tone and was of good quality.

Example VI

A copy made by the direct method of Example I using a copy sheet coated with a 10% solution of copper chloride gave a yellowish green color, but a copy sheet made with 5% copper chloride and 5% nickelous acetate produced a legible gray copy.

Copies made with the same metallic ions used in Examples IV, V and VI by the reflex method gave similar results and therefore provided suitable means for achieving a variety of color with this method also.

It will be seen from the description of this invention that there is provided a method and articles of manufacture which achieve the objects stated for the invention. The process of this invention provides a rapid method for duplicating, a method which is particularly well adapted to the needs of so-called office duplicating. The process is flexible with respect to the types of originals which may be reproduced, and the colors in which the reproductions may be made. Moreover by the process of this invention there is produced copies which will withstand exposure to light, heat, moisture, and general rough handling.

I claim:

1. A method of reproducing copy from an original containing thereon indicia, capable of producing localized areas of heat, through a process of thermal reproduction, comprising the steps of

- (a) interposing a tissue sheet impregnated with dithioamide between said original and a copy sheet containing metallic ions capable of reacting with said dithioamide to form a water-insoluble chromophoric complex;
- (b) contacting said copy sheet, said tissue and said original; and
- (c) exposing the resulting assembly to a radiant flux of sufficient intensity and duration to generate in said indicia sufficient localized heat to sublime at least a portion of said dithioamide corresponding in area to said indicia and in direct proportion to the ability of said indicia to absorb and transmit heat, whereby said dithioamide is transferred to said copy sheet to react with said metallic ions to form on said copy sheet colored indicia corresponding to the indicia on said original.

2. A method in accordance with claim 1 wherein said metallic ions are nickel.

3. A method of forming a master tissue from which copies may be made from an original containing thereon indicia, capable of producing localized areas of heat, through a process of thermal reproduction, comprising the steps of

- (a) interposing between said original and a master receptor tissue a tissue containing dithioamide thereby to form an assembly comprising said original, said master receptor tissue and said dithioamide-containing tissue in intimate surface contact; and
- (b) exposing said assembly to radiant flux of sufficient intensity and duration to generate in said indicia sufficient localized heat to sublime at least a portion of said dithioamide corresponding in area to said indicia on said original and in direct proportion to the ability of said indicia to absorb and transmit heat whereby said dithioamide is transferred to said master receptor tissue to form a master tissue suitable for contacting with a copy sheet containing metallic ions which will react with said dithioamide

to form a water-insoluble chromophoric complex in said copy sheet.

4. A method of forming duplicate copies of an original containing thereon indicia, capable of producing localized areas of heat, through a process of thermal reproduction, comprising the steps of

- (a) interposing between said original and a master receptor tissue a tissue containing dithioamide thereby to form a first assembly comprising said original, said master receptor tissue and said dithioamide-containing tissue in intimate surface contact;
- (b) exposing said first assembly to radiant flux of sufficient intensity and duration to generate in said indicia sufficient localized heat to sublime at least a portion of said dithioamide corresponding in area to said indicia on said original and in direct proportion to the ability of said indicia to absorb and transmit heat whereby said dithioamide is transferred to said master receptor tissue to form a master tissue;
- (c) contacting said master tissue with a copy sheet to form a second assembly, said copy sheet containing metallic ions available for reaction with said dithioamide to form a water-insoluble chromophoric complex; and
- (d) heating said second assembly thereby to sublime a portion of said dithioamide to contact said copy sheet and react with said metallic ions therein thereby to form a duplicate of said indicia in said copy sheet.

5. A method in accordance with claim 4 wherein the step of heating said second assembly is accomplished by passing said second assembly through heated rollers.

6. A method in accordance with claim 4 wherein the step of heating said second assembly is accomplished by pressing said second assembly between heated platens.

7. A method in accordance with claim 4 wherein the step of heating said second assembly is accomplished by covering said second assembly with a radiant flux absorbing sheet and exposing the resulting assembly to radiant flux.

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