June 4, 1968 R. W. GUNDLACH ET AL 3,386,379

DUPLICATING WITH COLOR PRODUCING REAGENTS

Filed April 26, 1963 3 Sheets-Sheet 1

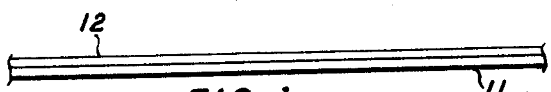


FIG. 1

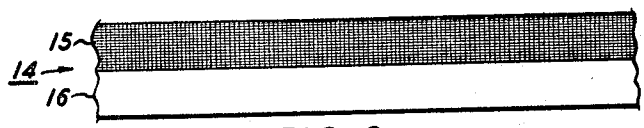


FIG. 2

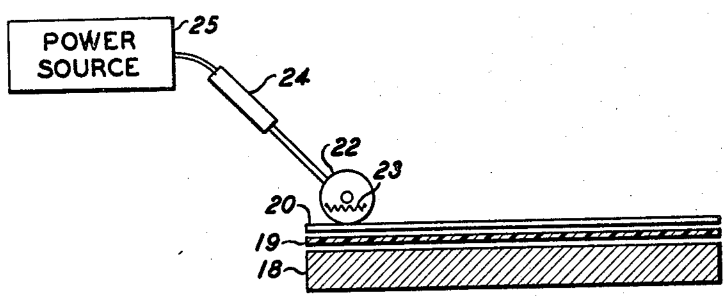


FIG. 3

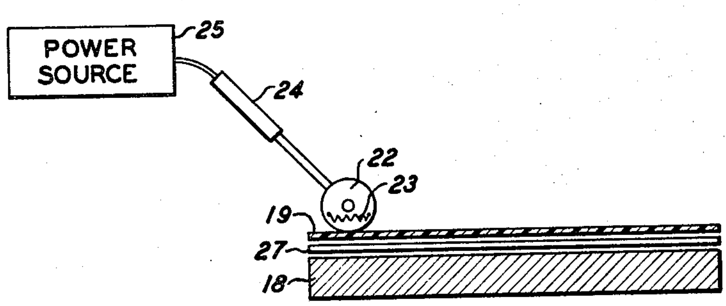


FIG. 4

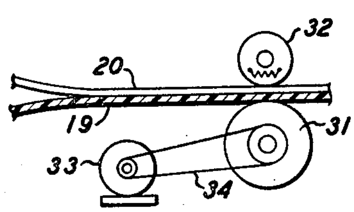


FIG. 5

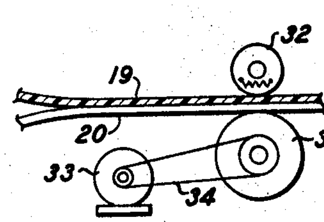


FIG. 6

INVENTOR.
ROBERT W. GUNDLACH
VSEVOLOD S. MIHAJLOV
BY
Stanley Z. Cole
ATTORNEY

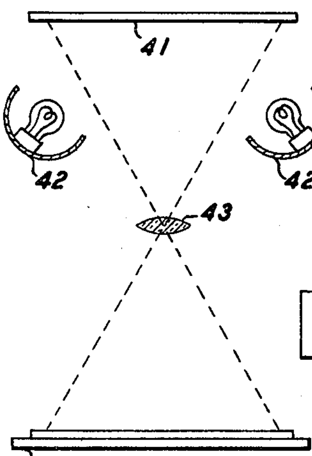


FIG. 7

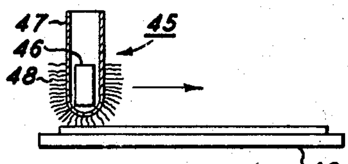


FIG. 8

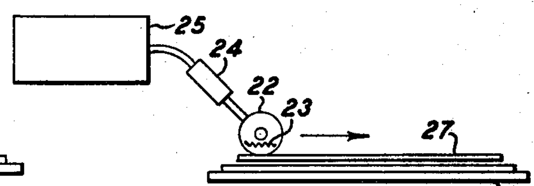


FIG. 9

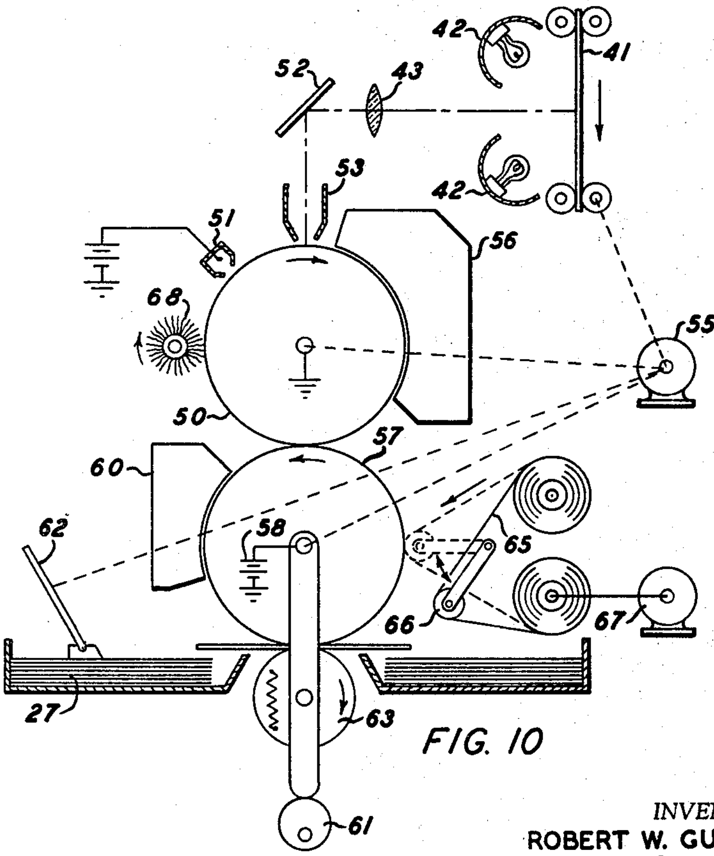


FIG. 10

INVENTOR.
ROBERT W. GUNDLACH
BY VSEVOLOD S. MIHAJLOV

Stanley Z. Cole
ATTORNEY

June 4, 1968 R. W. GUNDLACH ET AL 3,386,379

DUPLICATING WITH COLOR PRODUCING REAGENTS

Filed April 26, 1963 3 Sheets-Sheet 3

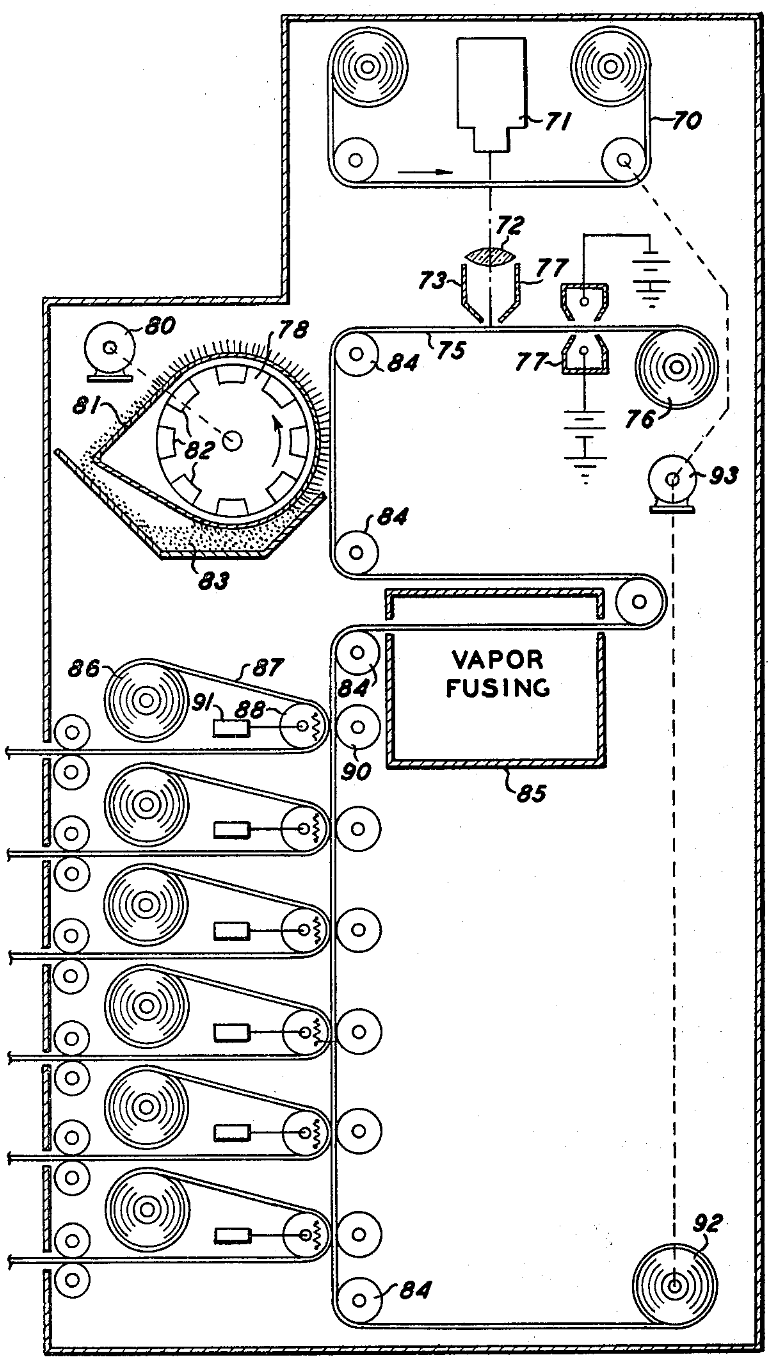


FIG. 11


INVENTOR.
ROBERT W. GUNDLACH
BY VSEVOLOD S. MIHAJLOV
Stanley Z. Cole
ATTORNEY

United States Patent Office

3,386,379

Patented June 4, 1968

1

# 3,386,379
# DUPLICATING WITH COLOR PRODUCING REAGENTS

Robert W. Gundlach, Victor, and Vsevolod S. Mihajlov, Rochester, N.Y., assignors to Xerox Corporation, Rochester, N.Y., a corporation of New York
Continuation-in-part of application Ser. No. 185,048, Apr. 4, 1962, now Patent No. 3,332,347. This application Apr. 26, 1963, Ser. No. 276,108
3 Claims. (Cl. 101—469)

This invention relates to duplicating processes and, in particular, to the making of duplicates of an original by the action of chemical reagents. This application is a continuation-in-part of application Ser. No. 185,048 filed Apr. 4, 1962, now U.S. Patent 3,332,347.

The tremendous amount of paper work involved in business and government administration today has produced a great interest in reducing the annoyance, time and expense of producing multiple duplicates of original copy by present methods. For example, it has been the common practice in clerical work to produce the desired number of copies using carbon paper. This not only increases the difficulty in handling but also makes it quite difficult to correct errors since each sheet must be corrected individually. Many duplicating machines are available for duplicating printed and other material by processes such as xerography, photo-copying, thermal and diazo processes. However, each of these processes require apparatus of some substantial complexity and/or expense. Less expensive duplicating processes such as spirit-duplicating processes and stencil-duplicating processes fall short of the desired characteristics on two points. Operators find that both of these are very messy so that ink or dye stains usually end up on the hands and clothes, and further that the copies made are very poor in image sharpness. This loss of sharpness in the case of spirit duplicating is due to slight bleeding of the dye due to the solvent action on the copy paper. In the case of stencil duplicating, bleeding occurs in the stencil due to the necessary characteristic of the stencil material required to permit passage of ink in the character areas.

Also, it is a common characteristic of the less expensive duplicating processes that they require some form of master or stencil which must be made up as by typing, handwriting, or in a way similar to that for making an original and is itself not suitable for use as an original document. The making of such stencils commonly adds all the disadvantageous effects that are found when using carbon paper in making duplicate copies. Now in accordance with the present invention, it has been found that by using color reagents and evaporation transfer techniques it is possible to greatly simplify low volume duplicating processes. One typewritten copy can be made using a color reagent and the color reagent can then be transferred to a duplicating master quickly, cheaply, and easily without any loss of quality in the typewritten original. Thus, the original remains available for use as an original copy and originals which are received are readily made into multiple copies without impairing the original, which in many instances must be preserved. In this manner, the use of carbon paper copies is avoided, the use of expensive duplicating equipment is avoided, and high resolution copies can be produced rapidly, cheaply, and neatly. Thus, it is an object of the present invention to define a novel copying process.

It is a further object of the present invention to define a dry vapor-thermographic duplicating process producing copies having high resolution.

It is a further object of the present invention to define means for producing multiple copies of an original by vapor-thermographic techniques.

2

It is a further object to define a method of producing a color reactive duplicating master xerographically.

Further objects and features of the invention will become apparent while reading the following description in connection with the drawings wherein:

FIG. 1 is a cross-sectional view of one embodiment of a typewriter ribbon carrying a color reagent;

FIG. 2 is a face view of a second embodiment of typewriter tape carrying a color reagent;

FIG. 3 is a diagrammatic illustration of simplified apparatus for carrying out one step of the inventive process;

FIG. 4 is a diagrammatic illustration of the simplified apparatus shown in FIG. 3 particularly illustrating a second step in the process;

FIGS. 5 and 6 are diagrammatic illustrations of rotary apparatus for carrying out the process steps shown in FIGS. 3 and 4, respectively;

FIG. 7 is a diagrammatic illustration illustrating exposure of a xerographic plate to an original;

FIG. 8 is a diagrammatic illustration of development of the xerographic plate using a color reactive developer;

FIG. 9 is a diagrammatic illustration of thermographic duplicating using the plate developed as in FIG. 8;

FIG. 10 is a diagrammatic illustration of duplicating apparatus in accordance with the invention;

FIG. 11 is a diagrammatic illustration of another embodiment of duplicating apparatus in accordance with the invention.

For simplicity of illustration, the invention will first be described using a typewriter to produce the original. As will be set forth below, however, this is only by way of example and the invention comprehends various other modes of producing the original.

In producing a typewritten original in accordance with the instant invention, the usual typewriter ribbon for a typewriter is replaced with a similar ribbon which has been inked with a conventional typewriter ink and also with a color reagent. This color reagent, which is herein termed "Chemical A," may be one of a number of chemicals for which a reaction partner exists so that when the two are combined, an intensely colored substance is formed. The reaction partner is herein termed "Chemical B." Following is a partial listing of suitable materials for Chemical A with corresponding reaction partners, Chemical B:

| Chemical A | Chemical B |
|---|---|
| (1) Pyrocatechol. | (1) Iron salts. |
| (2) Aniline. | (2) Vanadium salts. Potassium dichromate. |
| (3) Dithiooxamide. N-dimethyl-dithiooxamide. N,N'-bis(2-hydroethyl)dithiooxamide. N,N'-bis(carboxy-methyl)dithiooxamide. Other dithiooxamide derivatives. | (3) Copper salts. Nichel salts. Cobalt salts. |
| (4) Hydrazine. Pyrogallol. N-(p-hydroxyphenyl)glycine. Hydroxylamine. Diaminophenol hydrochloride. p-Methylaminophenol sulfate. Dichlorohydroquinone. Thiourea. Chlorohydroquinone. Bromohydroquinone. Gallic acid. Other organic reducing substances. | (4) Silver salts. |
| (5) Ammonia salts. Ammonium benzoate. Ammonium acetate. Ammonium carbonate. | (5) Organic diazonium salts and similar. |

As will be further described below, material typed using the ribbon containing Chemical A may be used to form a mirror-image master from which, in turn, multiple direct-reading copies may be produced on paper treated with the corresponding Chemical B.

FIGS. 1 and 2 show various embodiments of typewriter ribbon in accordance with the invention. In FIG. 1, the typewriter ribbon comprises support tape 11 carrying composition 12 of ink and an appropriate Chemical A. Support tape 11 can be any material suitable for use as a typewriter ribbon such as cloth fabric, metal foil, paper or plastic. Because non-uniformities are emphasized in a duplicating process, the support tape is preferably of a material that facilitates uniform typing. As is well known in the typewriter industry, greater uniformity is commonly achieved by using a non-reuseable ribbon. Such ribbons are conventionally referred to as "carbon ribbons" and use a thin plastic support tape. In a preferred embodiment, typewriter ribbon for use in accordance with the present invention comprises a polyethylene film coated with typewriter ink and Chemical A in which Chemical A is about 10–50% by weight of the ink and Chemical A mixture. Spray coating, roll coating, dip coating, evaporation coating, or other conventional coating means may be used. Alternatively, a cloth ribbon is saturated with an ink and Chemical A, of the same nature as for the plastic ribbon, by running the ribbon through a bath of the solution or by some similar process. For example, a silk typewriter ribbon dipped in a mixture of 20 grams rubeanic acid to 100 grams of black typewriter ink.

FIG. 2 shows an embodiment of a typewriter ribbon 14 in accordance with the invention in which one half of the ribbon 15 is coated or permeated with the ink and color reagent solution as in FIG. 1 and the other half of the ribbon 16 is coated with a chalk-like material for correcting errors. The correcting materials are selected for their ability to conceal a typed letter when the same letter is typed over with the error-correcting half of the ribbon, and further for their ability to form a vapor barrier so that no vapor can issue from the erroneously typed letter. For example, titanium dioxide or zinc oxide in a wax binder or the like have been found suitable for coating the correction half of the ribbon. Using a ribbon of the type illustrated in FIG. 2 and typing only a single copy increases ease of typing tremendously since the typist does not have to worry about material on carbon copies and, in correcting an error, does not have to use anything outside of the typewriter, itself, such as erasers or other materials available for correcting typewritten material. The typist merely backspaces, pushes the ribbon-position lever and retypes the letter in order to obliterate it. Thus, the typist's hands are not required to leave the keyboard of the machine in correcting errors.

In accordance with the invention, a single sheet of original typed copy is made using a ribbon in the typewriter corresponding to one of the embodiments illustrated in FIGS. 1 and 2. It is desirable that the typing be highly uniform in order to obtain good copies. Since the average typist does not have good uniformity of touch, an electric typewriter has been found preferable.

FIG. 3 shows a simple manually operated embodiment of apparatus to produce multiple copies of the typed original. This apparatus comprises heat conductive pad 18 such as will maintain a uniform low ambient temperature on its surface when a heated roller is rolled across a sheet of material resting on such surface. Thus, the heat conductive pad may be a metal such as aluminum having enough mass to absorb a considerable amount of heat without changing its over-all temperature by a significant amount. This pad should have a surface area adequate to support the largest size of copy sheet that may be desired. A rectangular size of about 10 x 15 inches is adequate for most purposes. The pad should preferably be not less than one quarter inch thick, but this is not limiting since the heat absorption and dissipation characteristics are controlling.

In accordance with the inventive process, master sheet 19 is positioned in contact with the surface of the heat conductive pad. This master sheet may be made of substantially any material that has a smooth finished surface such as a majority of plastic materials, metal foils, glass



or paper. By way of example, a 1 mil thick sheet of cellulose acetate has been used. Nonporous materials have generally yielded the best results but whether this is due to thermal characteristics, absorption characteristics, or some other characteristics is not fully understood at this time. Thickness of the master sheet is not critical and success has been obtained with sheets of 1 mil and of 15 mils thickness. The determining criteria relevant to this last characteristic are the amount of heat available and the permissible time for vaporizing volatile material from the surface of the master sheet. An excessive thickness will either act as a heat insulator or will dissipate the heat too rapidly for efficient operation. It is preferably less than about 10 mils thick so that it will not absorb or hold an excessive amount of heat. However, it can be much thicker than 10 mils; for example, a 3/32 inch thickness of window glass has been found suitable.

Typed original 20 is next placed face down against the smooth surface of the master sheet and heated roller 22 or other heat applicator such as a heat plate or heat lamp is used to apply heat against the back of typed original 20. Heat applicator 22, as illustrated, is a metal roller containing thermal element 23 which is connected through handle 24 of the roller to power source 25. In rolling the roller against the back of the typed original or in applying heat in one of the other ways suggested, the intensity of the heat and the length of time must be such as to cause a portion of Chemical A in the characters of the typed original to sublime or otherwise change to a vapor. Suitable heat may be applied by operating the roller at a temperature of about 200 to 400° F. and by rolling the heated roller across the back surface of original 20 at a speed of about ½ to 4 inches per second. With the roller at 240° a speed of about 1 inch per second has been used. These ranges have been found suitable using rubeanic acid as Chemical A. While still higher temperatures produce good results at faster speeds, such temperatures increase the likelihood of heat damage to the materials or equipment. Safeguards against such damage can be built in, but would increase expense. In the apparatus of FIG. 4, heat conductive pad 18 maintains master sheet 19 at a temperature relatively lower than that attained by typed original 20 when the heat is applied to it. Thus, a portion of the color reagent Chemical A is a transferred by vaporization and condensation from the typed original to the master sheet. Since the material thus transferred is transferred between surfaces that are in virtual contact, there is no significant loss of resolution. Since the amount of liquid transferred is very minute, bleeding effects are practically nonexistent.

After the color reagent, Chemical A, has been thermographically transferred to master sheet 19 as described above in connection with FIG. 3, the master sheet is removed from pad 18. Then as illustrated in FIG. 4, copy sheet 27 treated with Chemical B is positioned on pad 18 with its treated surface facing away from the pad. Copy sheet 27 may comprise any ordinary paper which has been chemically treated in accordance with the invention. Preferably, the paper is smooth surfaced to permit a more uniform contact in the duplicating process. If the color reagent, Chemical A, is dithiooxamide, otherwise known as rubeanic acid, the copy paper is appropriately treated with a coating solution of, for example, nickel salts dissolved in water, alcohol or similar solvent to a solution of 5% to 25% by weight volume. For improved density, it has been found advantageous to add an amine in which one or more hydrogen atoms attached to nitrogen have been replaced by one or more alkanol groups. A suitable amount of this additive has been found to be 0.5 to 4.0 moles per mole of nickel. This additive is also advantageously used with the other metallic salts listed under Chemical B. One coating solution used is a 25% solution of $NiSO_4 \cdot 6H_2O$ containing two moles of 2-(2-aminoethyl) aminoethanol per mole of nickel. A solution of 25% weight by volume of copper sulfate in water has also produced effective results. The solution may then be coated on the paper by spraying, dipping, flowing, rolling, wiping or similar process. Some moisture content in the copy paper has been found to increase density further. Thus casein coated papers or paper treated with a humectant such as a sorbitol or glycerine have been found advantageous.

With the treated paper lying face up on the pad, master sheet **19** is positioned in face-to-face contact with the copy sheet so that the image-carrying surface of the master sheet is in contact with the treated surface of the copy sheet. Now, when heated roller **22** or similar heat applicator applies heat to the free surface of the master sheet, a portion of the color reagent, Chemical A, in character configuration on the master sheet is transferred by evaporation and condensation to the surface of the copy sheet. Where Chemical A contacts the copy sheet, it reacts with its reaction partner, Chemical B, on the copy sheet to produce a visible image.

Since transfers by the process described above are always by face-to-face contact in the embodiments described above and since the colored product is insoluble preventing bleeding, a very high resolution is obtainable in the copy.

In a further embodiment of the invention, it is possible to eliminate master sheet **19** described in FIGS. 3 and 4, but with a slight loss in resolution. In this further embodiment, treated copy sheet **27** is placed with its treated surface adjacent to the surface of pad **18**. Then typed original **20** carrying Chemical A in its typed characters, is positioned with its typed surface adjacent to the untreated surface of copy sheet **27**. When heat is applied as by roller **22** or other heat applicating means, Chemical A vaporizes and condenses on copy sheet **27**. If copy sheet **27** is made of a very porous paper or paper-like material, some of the vapor will pass through the pores reaching the treated surface of the copy paper. Otherwise, Chemical A should be chosen as a material that does not sublime but passes through a liquid phase. When this material condenses as a liquid on the untreated surface of the copy sheet, it is absorbed by the copy sheet and passes through in order to react with the reaction partner, Chemical B, on the opposite surface of the copy paper. As is apparent, in order to maintain an acceptable level of resolution, the copy paper in accordance with this embodiment should preferably be quite thin—in the nature of a mil or less. However, thicker copy papers may be used with the attendant disadvantage of slightly lower resolution. A second method for going directly from original to copy requires the use of substantially transparent copy sheets. The transparent copy sheet carrying Chemical B is positioned with its coated surface facing the typed surface of the original. The two are heated causing vaporization and chemical reaction on the contact surface of the copy sheet. The image is then directly readable through the reverse side of the copy sheet.

FIGS. 5 and 6 show an embodiment of simple rotary apparatus for performing the process illustrated in connection with FIGS. 3 and 4. In this embodiment, cylinder **31** and cylinder **32** perform the functions of pad **18** and roller **22**, respectively, of FIG. 3. It is considered preferable that one of the cylinders have a slightly yieldable coating and high friction qualities. For example, covering one cylinder with a surface layer of silicone rubber has been found advantageous. Thus, cylinder **32** is a heated cylinder. In this embodiment, the thermal characteristics of cylinder **31** are not particularly critical. However, it has been found that cylinder **31**, because of its close proximity in operation to cylinder **32**, is ihclined to draw heat from cylinder **32** reducing its temperture and causing non-uniform heat distribution. Thus, it is preferable to heat cylinder **31** as well as cylinder **32** as illustreated by thermal elements **23**, or to cover cylinder **31** with a heat insulating layer so as to reduce heat dissipation. Good results have also been obtained by heating



only cylinder **32**, but maintaining the two cylinders in continuous rotating contact for an extended period prior to use so as to reach a point of temperature stability. With the temperature on heated cylinder **32** stabilized in the range between 200 and 400° F., master sheet **19** and typed original **20** are run in between cylinders **31** and **32** and advanced by rotation of the cylinders. Motor **33** is illustreated as driving cylinder **31** through drive means **34**. However, it should be understood that the same operation can be performed by a manual crank. As the two sheets run between the two cylinders, heat from heated cylinder **32** penetrates to the characters in the typed original and causes the color-reagent Chemical A to vaporize into the minute space between the two sheets. It is pointed out that this minute space is the natural result of positioning two smooth sheets in contact. A mere positioning of two sheets in contact in this manner even when they are run between pressure rollers will not eliminate all space between the contacting surface. Minor variations always present in such surfaces prevent complete elimination of such space. As the two sheets pass between the two cylinders, some Chemical A is transferred to the master sheet. The image on the master sheet is commonly a weakly visible image.

While not necessarily limiting as to how the transfer of Chemical A actually takes place, it is theorized that it vaporizes due to the heat between the two sheets and then as the two sheets issue from between the cylinders, they are cooled by the ambient temperature of the air so that condensation or sublimation of Chemical A occurs in part on both surfaces. It has been found that transfers of Chemical A to the master sheet have consistently attained levels of 75% or more transfer. While the reason for this is not completely understood, it is possibly due to the use of master materials which are relatively more heat conductive than the paper used for the original. This would allow the master to cool faster and thus condense the evaporated chemical at a higher rate than the original. It should be noted that in this embodiment there is no requirement as to whether the master sheet or the typed original is in direct contact with the heated cylinder. It is only necessary that enough heat be applied to one or the other so that heat penetrates the sandwich and volatilizes some of the color reagent.

Next, as illustrated in FIG. 6, a treated copy sheet is positioned with its treated surface in contact with the surface of the master sheet now carrying transferred Chemical A in the mirror image configuration of the original. The two sheets are advanced as a sandwich between cylinders **31** and **32** in a second vaporthermographic transfer process similar to that illustrated in FIG. 4. Again the heat may be applied to either surface of the sandwich so long as it is adequate to cause vaporization of some of the Chemical A present on the master sheet. As the two sheets pass between the cylinders, Chemical A is transferred to the copy sheet. While the apparatus of FIGS. 5 and 6 is capable of considerably more automation than that of the highly simplified apparatus illustrated in FIG. 3, it still requires a large extent of manual operation.

While the illustrated embodiments of FIGS. 1–6 have been described generally in relation to the reproduction of type-written material, the invention is in no way limited to typewritten material. Handwritten material using a pen or machine drawn material using some form of stylus device, in which the pen or stylus uses a drawing solution containing color reagent Chemical A, is suitable as an original for reproduction in accordance with the inventive process. A useable original may also be produced by xerography from an original that does not contain a volatile color reagent. Such a xerographic copy for use as an original in the inventive process would be made using Chemical A in a developer material for the xerographic image. It has been found for example that rubeanic acid, itself, will act as a suitable toner in developing an electrostatic latent image in the xerographic process. Thus, FIGS. 7–11 illustrate embodiments of the invention in which the duplicating master containing Chemical A has been formed xerographically.

FIGS. 7–9 are greatly simplified illustrations roughly comparable to FIGS. 1–4 but using a xerographic process rather than a typewriter for forming the duplicating master. FIG. 7 illustrates exposure of xerographic plate **40** to a light pattern from original **41** using light source **42** and lens **43**. While greatly simplified for illustrative purposes, this figure is meant to represent conventional formation of a xerographic latent electrostatic image in which a xerographic plate is electrostatically charged in the dark and then selectively discharged by a light pattern.

Plate **40** carrying the latent electrostatic image formed in FIG. 7 is then developed by a developing device **45** as illustrated in FIG. 8. The developing device illustrated in FIG. 8 represents a device known to the art as a magnetic brush. As illustrated, this comprises a magnet element **46** enclosed in a non-magnetic envelope **47**. The "brush" **48** is formed of ferromagnetic particles which form brush-like bristles under the influence of the magnet. For xerographic development, a pigmented developing "toner" is mixed in with the ferromagnetic particles before formation of the "brush." The mixture is known as a "toner-carrier" developer in which the relatively large ferromagnetic particles "carry" the smaller toner particles by virtue of triboelectric attraction. It is necessary that the toner material be widely separated in the triboelectric series from the ferromagnetic particles in order to obtain triboelectric attraction and charging between the toner particles and the ferromagnetic particles. It has been found that rubeanic acid itself, in its common commercial powder form, is suitable with conventional magnetic brush carrier particles such as described in U.S. Patent 3,015,305. Conventional resin toner can be added along with the rubeanic acid to enable fusing of the image. Rubeanic acid toner can also be produced by the same technique as conventional xerographic toners, substituting the rubeanic acid for the carbon black or other pigment. Where a good visible xerographic image is desired, both conventional pigment and rubeanic acid may be added together. Resin material in the toner helps control the evaporation of the rubeanic acid in the duplicating process permitting greater uniformity over a larger number of copies and has also been found to reduce "ghosting." While FIG. 8 illustrates magnetic brush development, other forms of xerographic development such as cascade and powder cloud development are equally operable.

The developed image on the xerographic plate can be used in a direct thermographic transfer to a metal salt treated copy sheet **27** as illustrated in FIG. 9. Treated copy sheet **27** is positioned on top of the duplicating master and heated roller **22** is passed over the back of copy sheet **27** so that heat from the roller passes through sheet **27** and heats the image material on the surface of the xerographic plate causing some of Chemical A to evaporate and react with Chemical B on the copy sheet **27**. As illustrated in FIGS. 7–9, a mirror reverse image would be formed on the xerographic plate so that a vapor thermographic transfer directly to a treated copy sheet, produces a direct reading image. However, to preserve the xerographic plate, it may be desirable to form a direct reading image on the xerographic plate by the addition of a mirror in the exposure system of FIG. 7 and then after development, transferring the image containing Chemical A in a conventional xerographic transfer process to an intermediate duplicating sheet or web which in turn is run against the treated copy paper for multiple duplication. The addition of a mirror permits forming a direct reading copy on the xerographic plate so that upon transfer to an intermediate master, a mirror image is obtained on the master suitable for making direct reading copies on the treated copy paper.

Complete system apparatus using a mirror and an intermediate master is illustrated in FIG. 10. FIG. 10 illustrates apparatus suitable for performing all of the operations from the original through to the multiple copies on metal salt treated paper. Xerographic drum **50** is electrostatically charged by charging device **51** and exposed to a light pattern of original **41** by means of lens **43**, mirror **52** and projection slit **53**. Original **41** and drum **50** are moved synchronously in accordance with slit projection techniques by motor **55**. After exposure, xerographic drum is developed with developer material containing Chemical A in a developing system depicted as cascade development means **56**. The developed image is transferred to intermediate duplicating drum **57** under the influence of a transfer potential applied to drum **57** by means of voltage source **58**. While not necessary for operability of the system, image fusing means **60**, depicted as a vapor fusing chamber can be used for liquifying and fusing resin that may be mixed with Chemical A in the developer. Vapor fusing, in accordance with this invention, has the advantage in that it does not vaporize or evaporate Chemical A as would heat fusing. As set forth above, the use of some amount of resin toner along with fusing improves the uniformity of reproduced copy but has some disadvantage in the present embodiment in making it more difficult to clean the intermediate master for reuse. Where resin and fusing is used, the intermediate master is preferably coated with a relatively nonporous material such as polytetrafluoroethylene or polyethylene terephthalate. During transfer of the image from xerographic drum **50** to intermediate master **57**, intermediate master **57** is supported firmly against drum **50** as by cam **61** positioned as illustrated. After transfer of the image to intermediate master **57**, cam **61** is rotated to separate the xerographic drum from the intermediate master. Treated copy sheets **27** are then fed by a feed dog **62** between the intermediate master **57** and a heated roller **63** producing multiple copies of the original. With the xerographic drum separated from the intermediate master during duplicating, the final run-off can be operated at a higher speed independently of speed limitations in the formation and transfer of the xerographic image. After the desired number of copies have been run off, cleaning web **65** is brought into position against the intermediate master by means of pivot roller **66** in order to clean residual image material from the intermediate master. The cleaning web **65**, such as described in U.S. Patent application S.N. 77,922 filed Dec. 23, 1960, is operated by a motor **67** and is preferably run in a reverse direction from the rotation of the master for optimum cleaning. Before forming a new xerographic image, drum **50** is cleaned by cleaning brush **68**.

While involving expense in consumable materials, some simplification can be derived from using the same material both as the xerographic plate and as the duplicating master. Preferably, such a material is of the nonreuseable variety which may be discarded after use. For this purpose, a xerographic grade of zinc oxide in an insulating resin binder coated on paper is conventional and available commercially. A particular advantage in a system using zinc oxide binder paper is that cleaning is unnecessary and ghosting problems are greatly reduced. An embodiment of apparatus suitable for utilizing a nonreuseable xerographic sensitive material is illustrated in FIG. 11. By way of example, the original to be reproduced is depicted as reel of microfilm **70** from which a light pattern is projected by means of light source **71**, lens **72** and exposure slit **73** to form a latent electrostatic image on xerographic web **75** which is suitably a zinc oxide binder paper. Web **75** is fed from supply reel **76** through charging device **77** past exposure slit **73** to magnetic brush developing device **78**. Magnetic brush developing device **78** carrying a magnetic brush of ferromagnetic carrier particles, resin and Chemical A, is rotated in a direction reverse to the web movement by a motor **80** against web **75** and then carries the brush material along the surface of nonmagnetic shield **81** until the ferromagnetic particles fall out of the influence of magnetic elements **82** so that the brush is disrupted and the developing material falls back into the developer compartment **83** from which a new brush is formed. Web **75** supported on rollers **84**, is carried after development into vapor fusing chamber **85** where the Chemical A and resin material is fused to enable greater uniformity in the following duplicating steps. Web **75** leaves fusing means **85** to pass through a selectable number of copying stations. Each copying station comprises a feed roll **86** for metal salt treated paper **87** and heated roller **88** for pressing paper **87** against web **75** while applying heat. Back up rollers **90** are provided at each duplicating station. Solenoid actuated positioners **91** are connected to each of heated rollers **88** to enable selectable operation of each of the duplicating stations. For example, if only one duplicate copy is desired, the solenoid **91** will be actuated in each duplicating station except one in order to retract the heated rollers preventing operation of the duplicating stations. After passing through the duplicating stations, web **75** is wound up on take up reel **92**. Movement of web **75** and movement of the original to be reproduced are operated synchronously by means of motor **93**. The web **75**, after being wound up on take up reel **92**, can be reused at a later time for running off further copies. For example, a sheet representing a particular page of copy may be cut off the reel of used web and mailed with or without duplicating copies so that further copies may be run off from it at a distant location.

In the disclosed embodiments, the source of heat while generally described as a heated roller or cylinder is not limited to such but can be any source of heat capable of supplying the necessary heat to cause vaporization of Chemical A. Thus, photoflash lamps, infrared lamps, any source of intense radiant illumination, sources for supplying hot air by blowers or convection currents and various electrical heating means are all contemplated as useable with the present inventive process. Various available machines may also be used such as the thermal processing machines available under the trade name, Thermo-Fax, available from Minnesota Mining and Manufacturing Company of St. Paul, Minn., and the thermal processing machines available under the trade name Kalfax, available from the Kalvar Corporation of New Orleans, La.

While the present invention has been described as carried out in specific embodiments thereof, there is no desire to be limited thereby, but it is intended to cover the invention broadly within the spirit and scope of the appended claims.

What is claimed is:

**1.** A method of image duplicating from a xerographic master which comprises forming an electrostatic latent image on the surface of a xerographic plate, developing said latent image with a toner composition comprising a thermoplastic material and a vaporizable color producing reagent, contact in the presence of heat said developed image with the surface of a salt treated copy paper such that a portion of said color producing reagent vaporizes and reacts with the salt component of said copy paper to produce a visible image.

**2.** The process as described in claim **1** wherein said color producing reagent is a dithiooxamide derivative and said salt is a metal salt.

**3.** The process as described in claim **2** wherein said dithiooxamide derivative is rubeanic acid and said metal salt is at leats one sulphate selected from the group consisting of sulphates of nickel, copper and cobalt.

**References Cited**

UNITED STATES PATENTS

| | | | |
|---|---|---|---|
| 2,582,932 | 1/1952 | Lustbader | 101—149.4 |
| 3,122,093 | 2/1964 | Lynch et al. | 101—149.4 |
| 2,889,758 | 6/1959 | Bolton | 95—1.7 |
| 3,115,814 | 12/1963 | Kaprelian | 95—1.7 |
| 2,297,691 | 10/1942 | Carlson | 101—149 X |
| 2,936,707 | 5/1960 | Maguire et al. | 101—426 |
| 3,054,692 | 9/1962 | Newman et al. | 101—426 |
| 3,094,417 | 6/1963 | Workman. | |
| 3,280,735 | 10/1966 | Clark et al. | 101—149.4 |


DAVID KLEIN, *Primary Examiner.*