

Feb. 21, 1961

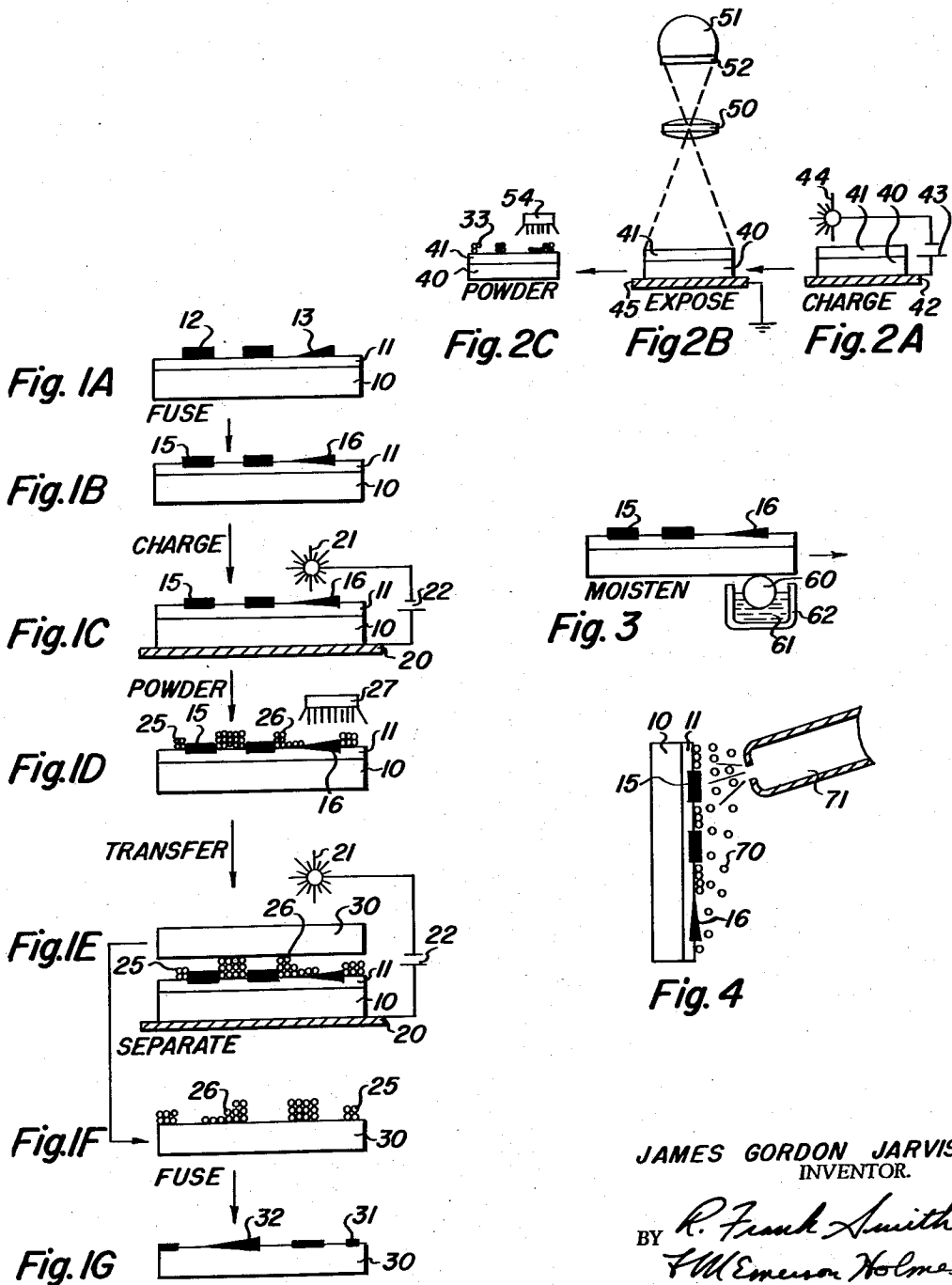
J. G. JARVIS

2,972,304

ELECTROSTATIC PRINTING

Filed June 2, 1959

3 Sheets-Sheet 1



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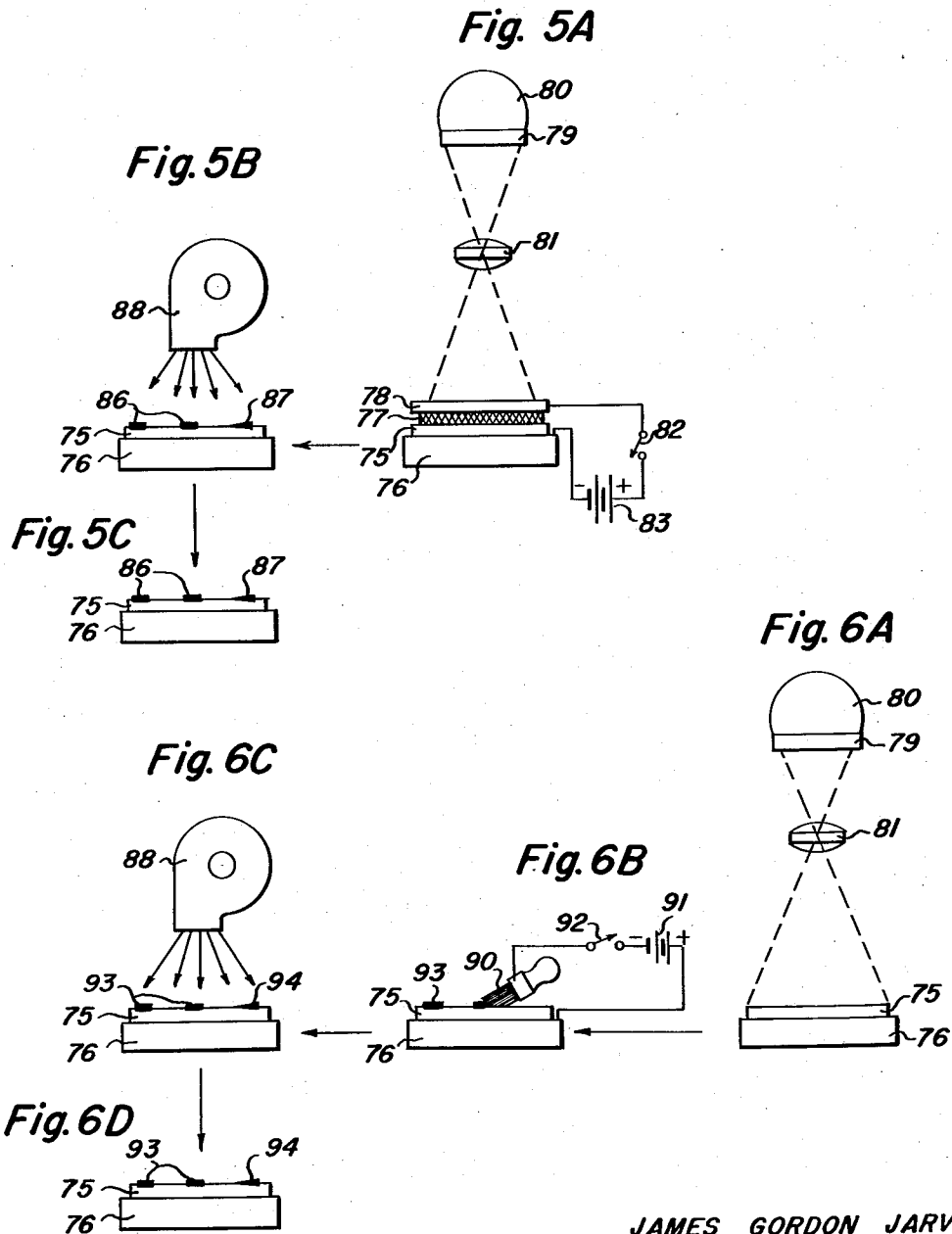
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Fig. 7

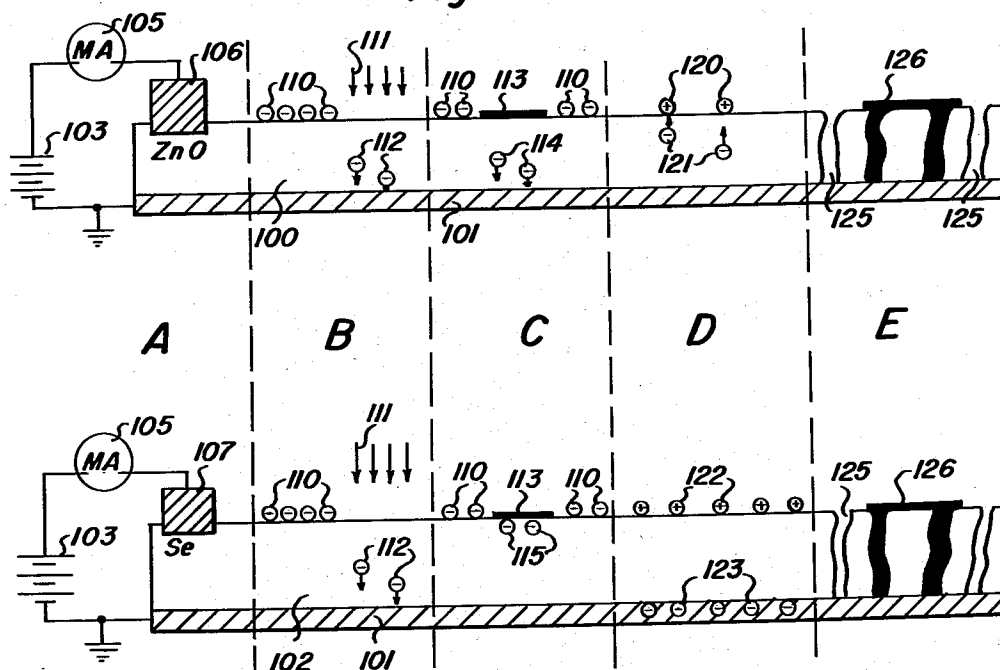


Fig. 8

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2,972,304

ELECTROSTATIC PRINTING

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1 Claim. (Cl. 101—426)

This invention relates to electrostatic printing. This is a continuation-in-part of my application Serial No. 614,636, filed October 8, 1956, now abandoned.

The invention is not directly concerned with electrophotography although electrophotography is one of the methods which may be used in preparing the printing plate. Rather, the invention is concerned with a method of making a succession of prints by applying a powder (pigment) to a printing plate and then transferring it to paper.

Also, special care should be taken not to confuse the invention with an unusual but nevertheless known form of electrophotography in which an electrostatic image is printed by contact (rather than projection) and by the electrostatic charging itself rather than by light. Like the ordinary electrophotography and photoconductography methods discussed below, this special system may be used in preparing the printing plate for the present invention. The present invention has a number of very distinguishing features, however, even when compared to this unusual system. For one thing the present invention involves the attraction of uncharged particles to charged areas rather than repulsion of charged particles. For another thing it is a negative-positive process whereas electrophotography generally, the above-mentioned unusual electrophotography, and ordinary electro-printing are all direct positive processes.

It is the object of the invention to provide a negative-positive process of electropainting.

It is also an object of the invention to provide such a process which is simple to operate, inexpensive and yet capable of producing high quality prints.

The invention may be practiced with a printing plate made in various ways, the two preferred systems being xerography and photoconductography.

Photoconductography is here defined to include those photographic processes in which a current pattern formed by a photoconductive layer is used to form an image electrolytically either during or after exposure. Some processes of this type are disclosed in British 118,030, Von Bronk, British 464,112 Goldman, British 789,309 Berchtold and Belgian 561,403.

According to the xerographic embodiment of the invention, one starts with a photoconductive plate, i.e., a conducting support (such as paper) and a photoconductive layer thereon such as a layer containing zinc oxide. A powder image (negative relative to the print ultimately desired) is placed on the photoconductive layer by any standard method. For example, since the layer is photoconducting, the powder image may be conveniently prepared by electrophotography.

The electroscopic powder should have an electrical conductivity when fused greater than the dark conductivity of the photoconductive layer. Any carbon-in-resin powder will serve. For example, 200 grams Piccolastic Resin 4358A (Pennsylvania Industrial Chemical Corp.), 12 grams Raven Black Carbon (Binney and Smith), 12 grams Spirit Nigrosine SSB (National Aniline Div. Allied

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Chemical and Dye Corp.), and 8 grams Iosol Black (National Aniline Div.), ground, fused and reground to 200 mesh or finer serves admirably. The specific electrical resistance of the powder should be less than one-tenth that of the photoconductive layer when dark.

The powder image is then fused to the photoconducting layer. Whether some of the fused-in powder is actually reaching through to the paper or merely acts as if it were does not matter, in the case of photoconductive zinc oxide in binder. The image may be either halftone or continuous tone. The conductivity (and hence the rate at which an electrostatic charge leaks away) is proportional to the amount of fused image, providing no light is falling on the layer. When selenium is used, a perfect layer would be undesirable since, unlike zinc oxide, the excessive charge leakage is obtained only by having the fused toner reach through to the paper via imperfections in the selenium layer. In the xerographic embodiment photoconductive zinc oxide works whether perforated or not but selenium does not work unless there are perforations. On the other hand such imperfections are common in thin coatings of selenium.

According to the photoconductographic embodiment of the invention, a metal or other conducting image is deposited on a photoconductive zinc oxide layer by electrolytic action either during or immediately following exposure of the photoconductive layer. In both embodiments when zinc oxide is used a conducting image is placed permanently on the surface of the photoconducting zinc oxide layer whose specific electrical resistance when dark, is at least 10 times that of the image material. However, the image material is and remains essentially on the top of the zinc oxide layer. Also in the photoconductographic embodiment any perforations in the zinc oxide layer would tend to allow the electrolyte to reach the conducting base (usually metal foil in this case) which tends to short circuit the electrolyte. Thus certain precautions must be taken in the preliminary steps, but the present invention has to do with the printing step after the plate has been made by one of these known methods.

In each embodiment the plate (with its fused or plated image) is now charged and developed (powder applied) in total darkness or under safelight illumination to which the layer is insensitive. The step of applying powder (either when making the plate or when printing therefrom) may be done by any standard method, e.g., by magnetic brush or by creating a smoke or dust cloud. Any standard electroscopic powder serves for this printing operation—the conductivity thereof is not critical.

A receiving sheet of paper or other material is placed in contact with the powdered layer and the powder is transferred to the paper by any of the many known methods. For example the receiving sheet may be adhesive or transfer may be by pressure with or without heat or solvent, or electrostatic transfer may be used. In the electrostatic case, if both the support for the photoconductive layer and the receiving sheet are poorly conducting, a high tension wire of the same polarity as used in charging the plate may be passed over the receiving side of the sandwich or one of the opposite polarity may be passed over the support side of the sandwich. The first of these electrostatic alternatives also works with conducting supports and the latter with conducting receiving sheets. In any electrostatic embodiment the transferred powder is fused or pressed into the receiving sheet.

When the plate is prepared by the xerographic method, the electrical conductivity of the fused electroscopic powder determines the time-cycle of the printing operation. To obtain printed copy free of veiled highlights, one must delay the second application of powder until the charges on the fused powder have leaked away sufficiently to prevent the attraction of a transferable deposit of

powder in areas corresponding to highlights. For the electroscopic powder described above, a delay of 10 to 15 seconds is satisfactory. By increasing the carbon content, the delay period can be reduced. The upper limit of carbon content (at about 30% by weight) is reached when the powder ceases to be firmly anchored to the surface after the fusing step.

Since the first fusing operation (the one where the low resistance powder is fused to the photoconductive layer) tends to dry out the paper support, increasing its resistivity, it is preferable to moisten the paper support before charging the plate. The use of a metal plate in place of the paper support removes the need for such moistening, of course.

These precautions are not pertinent in the photoconductivity embodiment. In fact, the plate is usually quite moist after the image is electrolytically formed and should be dried or allowed time in which to dry before being used as a printing plate.

The invention will be more fully understood from the following description when read in connection with the accompanying drawings in which:

Figs. 1A to 1G constitute a flow chart of a process incorporating the invention;

Figs. 2A to 2C similarly constitute a flow chart of one method of preparing the element illustrated in Fig. 1A;

Fig. 3 similarly illustrates a step in a preferred embodiment of the invention coming between the steps illustrated in Figs. 1B and 1C;

Fig. 4 similarly illustrates a step of the invention alternative to that shown in Fig. 1D.

Figs. 5A to 5C constitute a flow chart of another method of preparing the master printing plate illustrated in Fig. 1B.

Figs. 6A to 6D similarly constitute a flow chart of still another method of preparing the printing plate illustrated in Fig. 1B.

Fig. 7 and Fig. 8 compare photoconductive zinc oxide with selenium.

Various methods of preparing a conducting image on a photoconductive layer are known. In Fig. 1A a paper (or metal) support 10 provided with a photoconductive zinc oxide layer 11 carries a conducting powder image made up of areas 12 and 13. The area 13 is shown as a graded area to illustrate the fact that the present invention is applicable to continuous tone reproduction as well as to halftone reproduction. Even in the embodiments which have this conducting powder image, it does not matter how this powder image is produced on the photoconductive layer and several different methods are known.

The invention works particularly well with a paper base 10 and a photoconductive layer 11 containing zinc oxide, in binder. Also, the type of powder used is important and the most important characteristic of the powder is its electrical resistance. The electrical resistance of the powder should be less than one-tenth of that of the photoconductive layer when dark. The next step of the invention, as shown in Fig. 1B, is to fuse the powder into the layer 11 forming a conducting image made up of areas 15 and 16. The powder does not tend to fuse all the way through the photoconductive layer 11 but the net result is the same as if it did fuse all the way through to the conducting paper 10. If selenium is used in place of the zinc oxide, the conducting powder must fuse (for example via imperfections in the selenium) all the way through to the conducting paper 10.

Fig. 1B illustrates the printing plate and the image areas 15 and 16 are conducting whether they are made by fusing a conducting powder deposited by the xerographic method or by direct plating of a metal by the photoconductographic method. In either case the conducting image does not actually extend through the photoconductive zinc oxide layer 11, but acts as if it did. There

are various theories for the effect of the conducting image. It is believed that, in the absence of any such image, but in the presence of a corona discharge, an electrically reversed unbiased blocking layer forms near or in the surface of the layer. On the other hand when the image material is present at the surface of the zinc oxide, between the corona and the body of the zinc oxide layer, it tends to destroy the electric blocking effect of the interface. If this is what happens, the charge received from the corona would thus be permitted a relatively rapid leaking off through the zinc oxide layer. In any case the difference between the image-bearing and the non-image-bearing areas, in the rate of decay in the charge deposited on the surface of the photoconducting layer leads, after charging, to a difference in charge remaining on the two types of areas.

After the conducting image is established on the layer 11 by either method, it is electrostatically charged in total darkness or under safelight illumination to which the photoconductive layer 11 is insensitive. The charging (by corona discharge) is shown in Fig. 1C in which the plate is moved along a metal plate 20 under a wire 21 held at high tension by means indicated schematically at 22. The operation shown in Fig. 1D is also carried out in total darkness or under the safelight. Powder is applied to the plate which has retained the charge only in the areas between the image areas 15 and 16. The powder is shown schematically at 25 and 26, the thickness of the layer 26 being inversely proportional to the thickness of the image area 16. This powder may be applied to the plate by any of the standard methods. Fig. 1D illustrates the powder being applied by a magnetic brush 27 which is a standard procedure in the electrostatic photography art. The electrostatic charge applied in Fig. 1C very quickly leaks off the image areas 15 and 16 but remains on the surface of the photoconductive layer 11 since the layer is effectively in the dark. The powder 25 and 26 is attracted to the charged areas.

The next step of the process, as shown in Fig. 1E, is to transfer the loose powder image 25 and 26 to a sheet of paper 30 which is laid on top of the powder image and the whole sandwich is again passed under the high tension wire 21. The image 25 and 26 adheres to the paper 30 and transfers with it as shown in Fig. 1F. This powder image is then fused to the paper 30 by the application of heat (or is pressed into the paper by passing between rollers in the known way) forming a continuous tone or halftone image made up of areas 31 and 32 as shown in Fig. 1G. It will be noted that the image on the paper in Fig. 1G is a negative of the image on the plate shown in Fig. 1A. Also the final image is laterally inverted compared to the image in Fig. 1A. Accordingly, the plate shown in Fig. 1A is made negative and laterally inverted relative to the desired print.

The plate shown in Fig. 1A can be prepared by any standard electrostatic printing method. For example, one such conventional arrangement is shown in Figs. 2A to 2C. A paper plate 40 with a photoconductive layer 41 thereon is placed on a metal plate 42 and passed under a high tension wire 44 to receive an electrostatic charge. The source of high potential is indicated schematically at 43. The charged plate is then illuminated by an image (negative relative to the print ultimately desired) projected by a lens 50. The image is that of a transparency 52 mounted in front of suitable lamphouse 51. The image falling on the layer 41 causes this layer to be conducting in certain areas allowing the electrostatic charge to leak away in these areas. The remaining areas retain their charge. Accordingly, a powder 33 applied thereto by magnetic brush 54, as shown in Fig. 2C, is concentrated in the charged areas and forms an image. Any of the known methods of developing the xerographic image may be used including development from a highly insulating liquid containing a suspension of charged particles. This image is the same as the transparency 52. That is, it is

positive relative to the transparency 52 and is oriented the same way as the transparency when viewed from the front. When the transparency 52 is actually a negative and is turned over so as to be laterally inverted, the required laterally inverted negative image is obtained at 33. Then, according to the invention, this image is fused all as described in connection with Figs. 1A and 1B.

Fig. 3 illustrates a highly desirable improvement on the simple system shown in Figs. 1A and 1B. The fusing operation to produce the fused image shown at Fig. 1B tends to dry out the paper support 10 so as to interfere with subsequent steps of the operation. Accordingly, the paper 10 may be moistened by any suitable means such as a roller 60 rolling in a water bath 61 carried in a suitable container 62. The plate 10 is then ready for the step shown in Fig. 1C. The photoconductographic system discussed below avoids the need for such moistening, since the conducting image is plated rather than fused.

In Fig. 4 the developer powder 70 is applied to the plate from a suitable gun 71. This arrangement is alternative to the magnetic brush application illustrated in Fig. 1D. Another common arrangement for applying powder consists of merely tilting a plate back and forth to cause the powder while in contact with relatively large carrier particles to roll across the charged surface.

Figs. 5A and 5B illustrate one of the many known photoconductography methods of producing a metal image on a photoconductive layer. In the arrangement shown, a layer 75 consists of zinc oxide in a suitable resin binder carried on a conducting support 76 which may be either a conducting paper or preferably a paper backed aluminum foil. An electrolytic layer 77 containing developer ions such as a silver or gold salt is in contact with the photoconductive layer 75. The layer 77 is usually moist but dry electrolytes may be used. The front electrode 78 of the photoconductographic sandwich may consist of conducting glass or other transparent conducting material. Zinc oxide rather than selenium is used in this photoconductographic embodiment since selenium will not operate efficiently in the later printing step unless it has imperfections through which the plated metal reaches the base 76 and if there were many such imperfections the electrolytes (if void) would short circuit to the base and produce inferior photoconductographic prints.

A transparency 79 illuminated by a light in a lamp house 80 is focused by a lens 81 through the layers 78 and 77 onto the photoconductive layer 75. While this image is on, a switch 82 in the schematically illustrated electric circuit, is closed thus applying potential from a D.C. source 83 across the electrolyte 77 in such a manner that the electrode 76 acts as a cathode and, in those areas of photoconductive layer 75 which are conducting, metal is deposited from the electrolyte 77. It is well known that metals and other conducting materials may be deposited in this way which constitutes a standard photoconductographic procedure. The image thus plated is illustrated in Fig. 5B at 86 and 87 to correspond to the images 15 and 16 of Fig. 1B. To speed up the preparation of this printing plate which is shown in Fig. 5C, a blower 88 preferably supplying warm air, is used to dry the recording material. The plate of Fig. 5C corresponds to that of Fig. 1B and is charged as illustrated in Fig. 1C. The remainder of the process is the same as shown in Figs. 1C to 1G.

Since the conductivity produced in a zinc oxide layer by exposure to light does not decay immediately when the light is turned off, but actually continues for an appreciable time, a post exposure electrolytic development is possible and because of the simplicity of operation it is often preferable. In Fig. 6A the zinc-oxide-binder layer 75 carried on the paper backed aluminum foil 76 is exposed to an image of the negative 79 formed by the lens 81. The exposed layer is then moved under a brush 90 (or roller) carrying the developer ions (i.e. wet with

electrolyte) and current is passed between the metal handle of the brush 90 and the conducting support 76. The potential is provided by a source 91 through a switch 92 which is closed during development. The metal shown at 93 and 94 is plated out onto the zinc oxide layer and again is preferably dried by warm air from a blower 88 to constitute an electrically conducting image corresponding to 15 and 16 shown in Fig. 1B. Again it is noted that the conducting image 93 and 94 is on top of the zinc oxide layer 75 and need not extend through the layer.

It is quite surprising that high resolution can be obtained with this system. In fact, even the centers of closed letters, such as the letter O, do not fill in, as might be expected. They come out quite clean. In fact, the quality is in general better than that obtained by the various electrostatic printing processes which are carried out in the light.

Just as the powder image (specifically an image corresponding to an electric circuit) may be transferred from support 10 in Fig. 1A to a copper clad insulator and fused to the copper to act as a resist when etching the copper (in the making of printed circuits) so the powder 25 may be transferred and fused to a copper clad plate for similar manufacture of printed circuits. In both cases the flexibility of the support is an asset in maintaining sharp definition of the circuit.

Figs. 7 and 8 illustrate zinc oxide and selenium layers in enlarged cross section, and both figures are divided into five areas A to E in order to compare the properties of these two materials. In Fig. 7 a zinc oxide layer 100 (in binder) is coated on a grounded metal base 101 and in Fig. 8 a selenium layer 102 is coated on the grounded metal base 101. If one passes D.C. current by means of a power source 103, and an essentially ohmic electrode 106 through zinc oxide the current may be measured by a microammeter 105. An ohmic electrode is one substantially free of surface or barrier effects, the electrode 106 may be of indium for example and the electrode 107 may be of gold. The photo current varies with the intensity of the light falling on the zinc oxide. When dark, the specific resistance of zinc oxide is approximately 10^{10} ohm-cm. The same test run with selenium indicates that the dark resistance of selenium is much higher; it is at least 10^{13} ohm-cm. The relatively low resistance of zinc oxide would indicate that an electrostatic charge placed on the surface thereof should leak away fairly rapidly even in the dark. However, as indicated in area B of the two figs., negative charges 110 placed on the surface of the zinc oxide do not tend to leak away until light or other radiation 111 falls on the zinc oxide causing the charges indicated at 112 to leak away to the grounded base plate 101. The operation in the case of selenium is exactly the same.

Thus far there appears to be no essential differences in the operation of the two photoconductors, except that it is surprising that the charges 110 remain on the surface of the zinc oxide in total darkness as long as they do. It is believed that the charges 110 are actually prevented by some surface or barrier phenomenon from entering into the zinc oxide. This is similar to the boundary effect found in the cathode in some electrolytic systems. In fact, when the charge is produced by means of negative corona (which is ionized air) this corona may be considered to be the cathode and the charge 110 could be considered to be the residual charge left on the boundary or surface after the cathode had been taken away. If, as shown in area C, an extremely thin metal layer 113 (which may be so thin that it is not even visible) is placed on the surface of the zinc oxide, this metal apparently, according to theory, penetrates or overcomes the barrier layer and prevents the formation of such a barrier layer when a negative charge is applied to the surface.

Thus the negative charges 110 stay on the surface, but even in the dark, the charges 114 tend to leak away to

the grounded base plate 101. In fact, the barrier-breaking or barrier-prevention layer 113 does not even have to be metal or other highly conducting material. Certain non-conductors interfere with the formation of the barrier effect and allow the charges to enter the zinc oxide and once they are in, they leak away to the base. Non-metallic barrier-breaking layers can be deposited by the photoconductographic method or by the xerographic method discussed above.

In Fig. 8 the charges 110 remain on the surface and even in the area where a metal 113 allows these charges to pass through itself, i.e. through the metal 113, they remain as shown at 115 at the surface of the selenium, since the selenium is in the dark. The property of selenium is purely photoconductivity or at least it does not exhibit the barrier effect observed with zinc oxide. As discussed above in the various embodiments of the invention, the overcoming of the barrier on zinc oxide by a thin metal or other material is essential to the present invention, whereas it is the simple photoconductivity of the zinc oxide which is used in the preliminary (xerographic or photoconductographic) step of preparing the metal image. The present invention has to do with printing from such an image.

The distinguishing property of zinc oxide also becomes apparent as illustrated in area D, when one attempts to put a positive charge 120 on the surface of the zinc oxide. It is dissipated very rapidly since the negative charges 121 from the base plate 101 rises quickly to the surface and neutralizes any positive charges even in the dark. However, in the case of selenium positive charges 122 remain on the surface since negative charges 123 in the base plate do not flow through the selenium 102 while dark. Selenium will hold either a positive or a negative charge on its surface. Photoconductive zinc oxide of the type normally used in electrophotography will hold a negative charge but will tend to lose a positive charge fairly rapidly.

Area E is included to explain why some photoconductive selenium sheets do not always behave as discussed above. If the zinc oxide layer 100 or the selenium layer 102 happens to be perforated with a multitude of small holes or cracks 125, these perforations have little effect on the charge-storing properties of the layer as long as the total area of the perforations is small compared to the area of the layer. On the other hand the application of even slightly conductive material 126 into these holes 125 and over the surfaces between the holes, serves to prevent charging of these material-bearing areas. Thus imperfect zinc-oxide-resin or selenium layers (as shown in area E) appear to act the same as zinc-oxide-resin does in area C. The xerographic methods of preparing a printing plate for the present invention results in a satisfactory plate on the zinc oxide in area C or on

the zinc oxide or the selenium in area E, because the xerographic image in all three cases allows the surface charge to leak away even in the dark. The selenium in area C, however, does not work nearly as well although it is difficult to state that there is absolutely no barrier effect with selenium or to produce a selenium layer having absolutely no imperfections. The photoconductographic method of preparing a plate for the present invention similarly works for zinc oxide in area C and, to the extent it is possible to produce the photoconductographic images on imperfect coating, it also works for both zinc oxide and selenium in area E, but the results are definitely inferior because of the low quality of the photoconductographic image, particularly when a wet electrolyte is used.

It is realized that all of this description in connection with Figs. 7 and 8, of the phenomenon involved, is purely theoretical and the theory is not relied on in connection with the present invention. However, the differences in the observed phenomena between zinc oxide and selenium are important in the present invention and the theory given here aids in understanding the phenomena. Furthermore, selenium is itself objectionable in most photoconductographic processes since it reacts with or is adversely affected by most electrolytes commonly used. Thus, although selenium with imperfections may be used when preparing a plate by xerographic methods, for use in the present invention, the invention, in practice, generally employs plates coated with photoconductive zinc oxide in suitable binder.

I claim:

In the art of electrostatic printing onto a receiving sheet from an insulating photoconductive zinc oxide layer carried on an electrically conducting support and having an image of electrically conducting material on the surface thereof opposite to the support, the steps comprising electrically charging the layer, in the absence of any substantial amount of radiation capable of rendering the layer more conductive, by positioning the layer near a charging source of one polarity, then still in the absence of any substantial amount of said radiation, applying to the layer a powder which is attracted and adheres only to the areas of the layer free of the conducting image material, bringing said receiving sheet and layer into contact with each other with the powder layer sandwiched therebetween, and positioning the sandwich of layer and receiving sheet near a charging source of said polarity to transfer the powder to the receiving sheet.

References Cited in the file of this patent

UNITED STATES PATENTS

2,575,881	Walkup et al. _____	Nov. 6, 1951
2,576,047	Schaffert _____	Nov. 20, 1951