Sept. 6, 1966 G. H. ROBINSON 3,271,146
XEROPRINTING WITH PHOTOCONDUCTORS EXHIBITING
CHARGE-STORAGE ASYMMETRY
Filed March 19, 1963

Fig. 1A

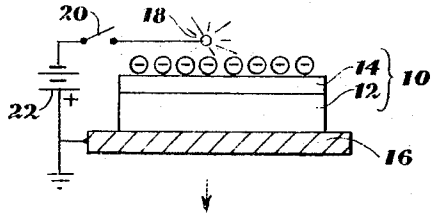


Fig. 1B

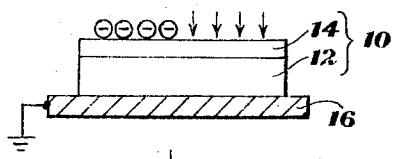
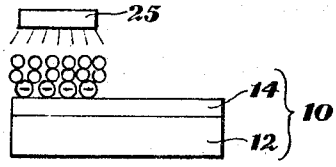


Fig. 1C



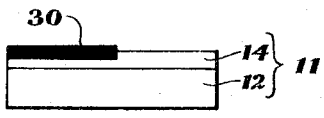
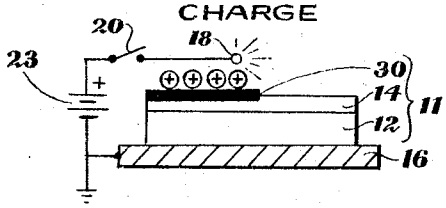


Fig. 1D

Fig. 2A



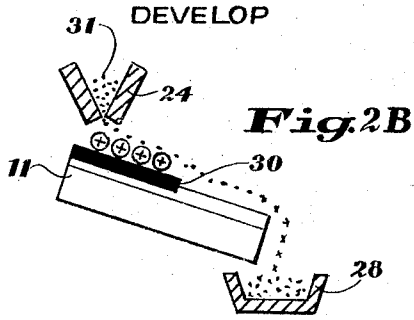


Fig. 2B

Fig. 2C

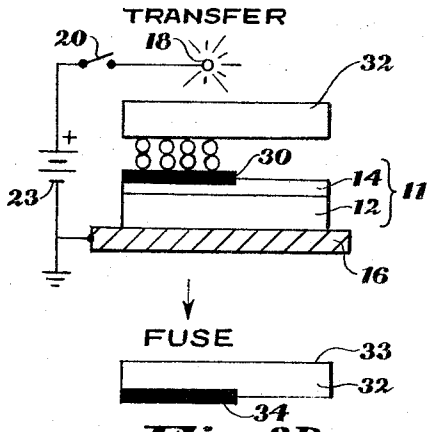


Fig. 2D

Gene H. Robinson
INVENTOR.
BY R. Frank Smith
Thomas R. Porter
ATTORNEYS

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XEROPRINTING WITH PHOTOCONDUCTORS EXHIBITING CHARGE-STORAGE ASYMMETRY

Gene H. Robinson, Rochester, N.Y., assignor to Eastman Kodak Company, Rochester, N.Y., a corporation of New Jersey

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8 Claims. (Cl. 96—1.4)

This invention relates to electrostatic printing and in particular to xeroprinting from a plate which is itself made xerographically and which is composed of insulating image areas on a photoconductor which exhibits charge-storage asymmetry.

In xeroprinting, a printing master, carrying on its surface complementary patterns of charge-storing and non-charge-storing areas, is repetitively cycled through the processing steps of charging, developing, and transferring to produce a plurality of copies. As is well known, the xeroprinting master may be prepared by manual methods such as painting or stenciling, by photographic methods such as the use of light-sensitive polymers, or by electrophotographic methods such as xerography or photoconductography.

The present invention relates to xeroprinting in which the printing master is prepared by electrophotographic methods. The invention relies on and, in a sense, compensates for, the charge-storage asymmetry property of many photoconductors, among which zinc oxide is an outstanding example. Zinc oxide of the type normally used in the preparation of xerographic layers has the property of being able to store, in the dark, large densities of negative charges for periods of many minutes or even hours, but of being unable to store appreciable densities of positive charges for even a few seconds. Another example of a photoconductor which displays charge-storage asymmetry is selenium. Selenium stores more positive charges for a longer time than it does negative charges. Certain zinc cadmium sulfide phosphors behave the same way.

According to the present invention a xeroprinting master is prepared by charging a photoconductive insulating layer which exhibits charge-storage asymmetry to a polarity which is easily stored, exposing it to a pattern of light, and developing the resultant electrostatic image with particles of matter which will permit these developed areas to store charges of the opposite polarity. In the printing operation, the master is charged to this *opposite* polarity, that is, to the polarity which is not readily stored by the photoconductor, but which is stored by the previously developed areas. It is immaterial, at least in the case of zinc oxide, whether this second charging operation is carried out in darkness or under illumination. However, as mentioned below, one object of the invention is to provide a process in which xeroprinting can be carried out in the dark, which is a very important advantage in practice. The electrostatic image so formed is developed with charged particles of matter which are then transferred to a receiving sheet and fused thereto by heat and/or pressure and/or adhesives to form a final, positive print. The developing step consists of the application of electrically insulating toner to the master, which toner becomes distributed in accordance with the electrostatic image. As is known in the art, the toner may have a polarity such as to adhere to either the charged or the uncharged areas of the master. The cycle of charging, developing, transferring, and fusing is repeated until the required number of copies has been obtained.

It is an object of the present invention to provide a positive-positive process of electroprinting.

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

It is a further object of the present invention to provide a xeroprinting process which may be carried out in complete darkness, and which is therefore well adapted to be carried out automatically in an enclosed cabinet which need not include a source of illumination.

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

FIGS. 1A through 1D constitute a flow chart of one method of preparing the printing master; and

FIGS. 2A–2D constitute a flow chart of the preferred embodiment of the xeroprinting process of the present invention.

As stated above, the only requirement of the insulating photoconductive layer used in the printing master in the present invention is that it display charge-storage asymmetry. Since zinc oxide is an outstanding example of a photoconductor having this property, the following description will relate to the use of zinc oxide.

FIG. 1 illustrates a xerographic process for the production of a xerographic print wherein the image is fused onto the xerographic layer. This layer is then used, according to the present invention, as the electrostatic printing master. FIG. 1A shows a xerographic plate **10** consisting of a paper or metal support **12** which is provided with an insulating photoconductive zinc oxide coating **14**. The xerographic plate **10** is laid on a grounded conducting backing **16**. The xerographic plate **10** is given a uniform negative electrostatic charge by means of a corona charger **18**, a switch **20**, and a power supply **22**. The xerographic plate **10** is then given an imagewise exposure, as shown in FIG. 1B, which discharges the electrostatic charge in the exposed areas and which leaves charges remaining in the unexposed or dark areas of the xerographic plate **10**. FIGURE 1C shows the next step of the process in which the electrostatic image is powder developed. The powder may be applied by any of the standard methods. FIG. 1C illustrates the powder being applied by a magnetic brush **25** which is a standard procedure in the electrophotographic art. FIGURE 1D shows the next step of the process in which the powdered electrostatic image is fused into the xerographic plate **10**, to produce a xerographic print which is used in the present invention as a xeroprinting master **11**.

The electrostatic printing process of the present invention, which uses a printing master consisting of insulating image areas on a photoconductive layer which exhibits charge-storage asymmetry, which master may be made by the process of FIG. 1, is described with reference to FIG. 2. FIG. 2A shows the printing master **11** laid on a grounded conducting backing **16**. A uniform positive electrostatic charge is applied to the printing master **11** by means of a corona charger **18**, a switch **20**, and a power supply **23**. The zinc oxide photoconductive layer **14** will not hold an appreciable positive charge and therefore the non-image areas of the printing master **11** do not become charged. The insulating image areas **30**, however, will hold the electrostatic charge. This charging step may be carried out in darkness or under illumination. FIG. 2B shows developer powder being applied to the printing master **11**. The developer powder **31**, which comprises negatively charged toner particles, is applied to the printing master **11** by means of a hopper **24**. The excess developing powder may be collected in a bin **28**. FIG. 2C shows the transfer of the toner particles, which have collected on the image areas **30**, to a transfer sheet **32**. Any of the known methods of transfer may be used; however, FIG. 2C shows an electrostatic transfer in which the receiving sheet **32** is given a uniform positive electrostatic charge by means of the corona charger **18**, the switch **20**, and the power supply **23**. FIG. 2D shows the final step of the process of the present invention in which the toner

particles which have been transferred to the receiving sheet **32** are fused thereto by the application of heat (or are pressed into the receiving sheet **32** by passing between rollers in the known way), forming a final print **33**. The print **33** having image areas **34** is a positive reproduction of the printing master **11**.

A reduction to practice of the present invention was carried out as follows.

Example No. 1

A ZnO photoconductive layer was uniformly charged to a negative potential and exposed by transmission to a wrong-reading positive transparency. The latent electrophotographic image was then developed with a magnetic brush of iron filings and a positive polarity dry toner composed of 50 parts D–125 Piccolastic resin produced by Pennsylvania Industrial Chemical Corporation, Clairton, Pennsylvania; 5.5 parts Iosol Black dye, and 1.2 parts Plasto Brown dye, both of which are manufactured by National Aniline Division of the Allied Chemical and Dye Corporation, Buffalo, New York. The xeroprinting master was then heat fused and recharged under a positive corona in the dark (the charging operation could just as well have been carried out under illumination). Since ZnO will not store an appreciable positive charge, the powdered characters were the only areas to become charged. The master was developed by cascading a developer consisting of a carrier bead and a negative polarity electroscopic powder over its surface. The toner powder on the developed areas was then electrostatically transferred to bond paper to which it was fused. Successive recharging and development steps were carried out to obtain the desired number of copies.

Example No. 2

A ZnO photoconductive layer was charged and exposed in the same manner as described in Example No. 1. The electrostatic image was developed with a liquid dispersion of .5 g. Sleight and Hellmuth 3046 yellow lithographic ink dispersed in 250 ml. of cyclohexane. The xeroprinting master was then processed as described in Example No. 1 to yield the desired number of copies.

As stated above, the present invention has been described with reference to the use of zinc oxide as the photoconductive material. Other photoconductors, for example, selenium or certain zinc cadmium sulfide phosphors, can be used. In preparing a xeroprinting master with them, they are positively charged, exposed, and developed with particles of matter which permit the developed areas later to store negative charges. For xeroprinting, the master is charged negatively in the dark, and developed with charged particles which are transferred to a permanent receiving sheet. Since these particular photoconductors do store some negative charges, it is necessary in order to obtain clean highlights or low background in prints, to provide a delay period of from a few seconds to several minutes to allow the photoconductor to lose its charge in the non-image areas. The bare photoconductor loses its charge at a greater rate than does the insulating material deposited on it in the first development. Alternatively, to obtain clean highlights one can, during development, balance out with electric bias fields the influence of these stored charges. Such stored charges can also be removed by illumination, but this is not necessary. There should be a difference in charge density between image and background areas corresponding to a difference in potential of about 50 volts. To realize the full optical density of most developers, however, there would have to be a potential difference of about 200 volts. The preferred embodiment using zinc oxide and positive charges does not require bias or a long delay or the use of light to enhance the conductivity.

While the present invention has been described with reference to the preferred embodiments thereof, it is not desired to be limited thereto but it is intended to cover the invention within the spirit and scope of the appended claims.

The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:

1. An electrostatic printing process comprising
uniformly applying to a photoconductive layer which exhibits charge-storage asymmetry, electrostatic charges of the polarity which said layer readily stores, in the absence of any substantial amount of radiation to which said layer is sensitive,
imagewise exposing said layer to cause the charges to leak away in the exposed areas,
applying electrically insulating toner to said layer whereby said toner becomes distributed in accordance with the electrostatic image,
fusing said toner to said layer to form insulating image areas,
uniformly applying to said layer electrostatic charges of the polarity which said layer does not readily store,
applying toner to the electrostatic image formed by the charges retained on said insulating areas,
transferring the last-mentioned toner from said layer to a receiving sheet, and
fusing said last-mentioned toner to said receiving sheet.

2. The process according to claim **1** in which the second step of uniformly applying electrostatic charges to said layer is carried out in the absence of any substantial amount of radiation capable of rendering said layer conductive to charges of the first-mentioned polarity.

3. An electrostatic printing process comprising
uniformly applying, to a xeroprinting master consisting of a xerographic print having insulating image areas on an insulating photoconductive layer which exhibits charge-storage asymmetry, electrostatic charges of a polarity which said photoconductive layer does not readily store,
applying toner to the electrostatic image formed by the electrostatic charges retained on said insulating areas,
transferring said toner to a receiving sheet, and
fusing said toner to said receiving sheet.

4. The process of claim **3** in which said step of uniformly applying electrostatic charges takes place in the absence of any substantial amount of radiation capable of rendering said photoconductive layer conductive.

5. In the process of electrostatic printing onto a receiving sheet from an insulating photoconductive zinc oxide layer having image areas of electrically insulating material on the surface thereof, the steps comprising
uniformly applying positive electrostatic charges to said layer,
uniformly applying toner particles to said layer whereby said toner becomes distributed in accordance with the electrostatic image,
transferring said toner particles to said receiving sheet, and
fusing said toner particles to said receiving sheet.

6. The process of claim **5** in which said step of uniformly applying positive electrostatic charges to said layer takes place in the absence of any substantial amount of radiation capable of rendering said layer conductive.

7. An electrostatic printing process comprising
uniformly applying to an insulating photoconductive zinc oxide layer, in the dark, negative electrostatic charges,
imagewise exposing said layer to cause the charges to leak away in the exposed areas,
applying electrically insulating toner to said layer whereby said toner becomes distributed in accordance with the electrostatic image,
fusing said toner to said layer to form insulating image areas,
uniformly applying to said layer positive electrostatic charges,

uniformly applying toner to the electrostatic image formed by the charges retained on said insulating areas,

transferring the last-mentioned toner from said layer to a receiving sheet, and

fusing said last-mentioned toner to said receiving sheet.

8. The process of claim 7 in which said step of uniformly applying positive electrostatic charges to said layer takes place in the absence of any substantial amount of radiation capable of rendering said layer conductive.

No references cited.

NORMAN G. TORCHIN, *Primary Examiner.*

J. T. BROWN, *Assistant Examiner.*