

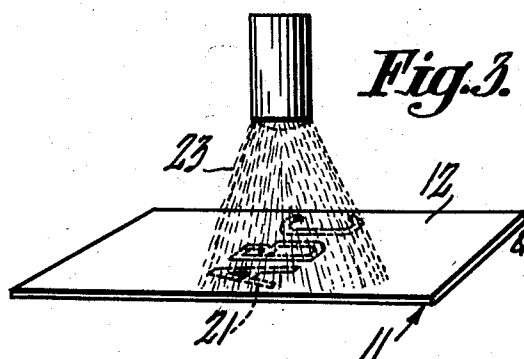
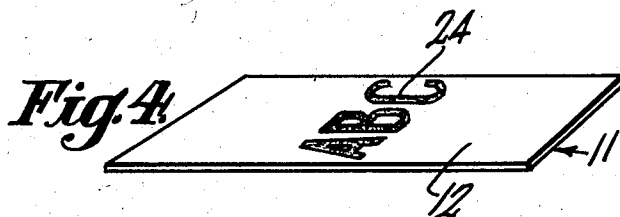
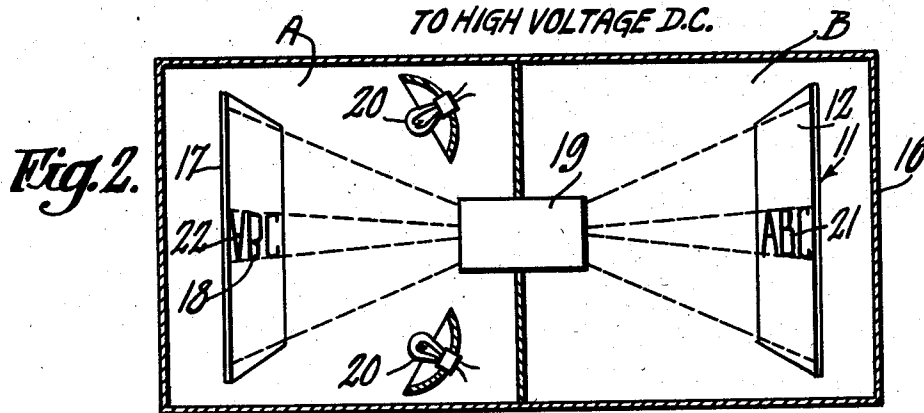
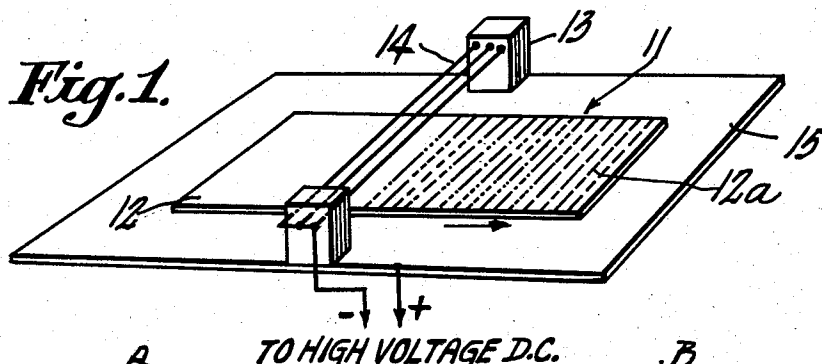
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ELECTROPHOTOGRAPHIC MEMBER

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ELECTROPHOTOGRAPHIC MEMBER

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5 Claims. (Cl. 96—1)

This invention relates to an improved process of forming images on a printing base. More particularly, the invention relates to an improved electrostatic printing process and to improved materials useful in this type of process.

An electrostatic printing process is that type of process for producing a visible record, reproduction, or copy, which includes, as an intermediate step, converting a light image or image signals into an electrostatic charge pattern or image on a printing base. The process may also include converting the electrostatic image into a visible image which may be a substantially faithful reproduction of an original except that it may be a different size. Alternatively, the visible image may be a series of characters corresponding to an intermediate optical or electrical image responsive to image signals received from some external source.

Certain previously proposed electrostatic printing processes utilize a conductive backing plate with a surface layer of photoconductive insulating material such as selenium, anthracene, or sulfur with the selenium being preferred. An overall electrostatic charge is provided on the surface layer. A light image is focused on the charged surface in order to discharge the portions upon which the light rays impinge, while leaving the remainder of the surface in a charged condition thereby forming a charge image. The charge image is developed by application of an electroscopic powder. Finally, a copy of the developed image is transferred to a sheet of paper or other material upon which the reproduced image is desired, and the transferred image is fixed.

Using the type of process above described, sharp reproductions can be obtained of line drawings, typewritten or printed matter, and the like. While such processes have the further advantages of simplicity of apparatus required and cheapness and ease of handling of the developing materials, they also have some inherent disadvantages. For example, it is necessary to make a transferable copy on the photosensitive plate first, in order to make a single final copy on paper. This is tedious, time consuming, and expensive when a large number of separate items are to be copied. Moreover, the photosensitive plate must be subjected to a special cleaning process after each exposure in order to remove the intermediate print, before the plate can be used for another subject. Also, after a relatively few uses, the photosensitive material becomes "fatigued" and either must be permitted to rest for a considerable period or must be regenerated. Thus where a large volume of work is to be handled, unless a method of regeneration is used, a number of photosensitive plates must be rotated in use. The photosensitive surface is also subject to wear in handling and use and must be repaired or renewed from time to time.

It is, therefore, highly desirable to eliminate the intermediate step of using a photosensitive plate having a conductive backing and to employ an electrostatic printing process involving direct reproduction on the final

2

surface. A direct reproduction process utilizing a printing base coated with a photoconductor such as zinc oxide suspended in a suitable vehicle has been described by H. G. Greig in U. S. patent application Serial No. 248,937, filed September 29, 1951, now abandoned, and now embodied in a continuation-in-part application Serial No. 383,677, filed October 1, 1953. However, a zinc oxide coated printing base, while satisfactory for certain uses has certain limitations.

The spectral response of white zinc oxide, for example, is confined essentially to the far blue and the ultraviolet. This limited spectral response limits the process using white zinc oxide to applications where the required radiation is available. The limited band of spectral response also limits the speed of response throughout the spectrum except in the ultraviolet. Furthermore, white zinc oxide mixtures prefer negative blanket charges and are not as satisfactory for positive blanket charges.

An object of the present invention is to provide an improved process of electrostatic printing.

Another object is to provide an improved reproduction process for copying printed or typewritten matter, half-tones and continuous tone images.

Another object is to provide an improved method and means of electrostatic printing having a spectral response which may be controlled over a broad range.

A further object is to provide an improved method and means of electrostatic printing having an improved speed of response in visible light.

Another object of the invention is to provide an improved method of preparing a printing base to receive an electrostatic charge pattern.

Another object of the invention is to provide an improved direct method of electrostatically printing on a printing base having a backing sheet made of paper or metal.

Another object of the invention is to provide an improved surface for receiving an electrostatic charge pattern.

A further object of the invention is to provide an improved surface for receiving an electrostatic charge pattern or image which can be developed to produce a visible image.

Still another object of the invention is to provide an improved process for converting an electrical signal into visible recorded information.

In accordance with the present invention, a surface of the backing sheet which is to receive the copy is coated with a composition comprising a colored photoconductor suspended in an electrically insulating, film-forming organic vehicle or binder thereby producing the printing base. The spectral response, the speed of response and the contrast characteristics of the printing base can be controlled by proper choice of the photoconductor and the vehicle. The colored photoconductors usually have their peak spectral response in the visible region although it may be anywhere between the far infra red and the far ultra violet. The color of the photoconductor indicates approximately the location of the absorption edge of the material and therefore indicates the spectral response of the photoconductor. The proper choice of one or more colored photoconductors produces a printing base having any desired spectral response from far infra red to far ultra violet, over as narrow or wide a band of frequencies as desired. Furthermore, it is possible to select a colored photoconductor which, suspended in a suitable vehicle or binder, has a desirable electric charge storage characteristic and a linear rate of discharge with intensity of illumination. This makes it possible to design printing bases which have any desired speed of response within certain limits and almost any desired contrast characteristics. The printing bases of

this invention can be designed to give faithful continuous tone reproductions of outdoor subjects in daylight. Colored photoconductor mixtures work equally well for positive or negative blanket charges. Hence either a positive or a negative visible image may be developed from the same incident light image by changing the polarity of the blanket charge.

A uniform electrostatic charge is applied to the coated surface and a light image of the matter to be reproduced is directed onto the charged surface causing a charge image to be formed which corresponds to the light image. This charge image may be stored for a time in the dark, if desired, or it may be immediately developed to render it visible. Development may be accomplished by applying to the paper an electroscopic substance such as a pigmented powder which adheres to the charged portions and does not adhere to the discharged portions. Alternatively, the developer powder may be one which adheres to the edges of the discharged portions of the charge image.

The objects of this invention will be more apparent and the invention will be more fully understood from the following detail description and the accompanying illustrative drawing of which:

Figure 1 is a perspective view of apparatus which may be utilized in carrying out the charging step of the process of the present invention.

Figure 2 is a view partially in perspective and partially in section, of apparatus which may be utilized in forming an electrostatic image on a printing base in accordance with the process of the present invention.

Figure 3 is a perspective view of simple means for developing an electrostatic image formed as shown in Figure 2, and

Figure 4 is a perspective view of a sheet carrying a developed image.

Similar reference characters are applied to similar elements throughout the drawings.

An important feature of the present invention resides in the printing base which is to receive an electrostatic charge pattern. The printing base is produced by coating a particular photosensitive composition on a surface of a backing sheet. Several examples of photoconductive printing bases of this invention will now be given.

Example 1.—100 grams of powdered lead iodide are mixed with 100 ml. of toluene and 60 ml. of a 60% solution of a silicone resin in xylene. This mix is ball-milled until the lead iodide is thoroughly dispersed in the plastic-solvent mix. The ball-milled suspension is coated on a surface of a sheet of paper by any of the standard paper coating techniques, for example, dipping, painting or spraying and then allowed to dry. The resulting yellow-orange coated paper is photosensitive through most of the visible and ultra-violet regions of the spectrum. The paper has a relatively high sensitivity and requires handling in the dark or under a deep red safe light during charging and development of the electrostatic image.

Example 2.—100 grams of C. P. grade finely powdered arsenic trisulphide are mixed with 100 ml. of toluene and 60 ml. of a 60% solution of a silicone resin in xylene. This mix is ball-milled and coated on paper in the same manner as in Example 1. The resulting bright yellow coated paper has a very high resistivity, a long charge-storage time and a relatively low sensitivity. Due to its relatively low sensitivity, the electrostatic printing process may be carried out in ordinary room light using a high intensity exposure from a blue or ultra-violet source to form the electrostatic image.

Example 3.—100 grams of finely ground cadmium selenide are ball-milled with 150 grams of a 35% polystyrene solution in toluene. This mix is coated on a metal backing plate as in Example 1. The resulting black coated sheet is panchromatically sensitive and may be used as in ordinary photographic processes. An image on this coating may be developed with a finely-divided white semiconducting powder, for example, magnesium silicate.

The backing sheet may be either a relatively insulating material, such as paper, or it may be an electrically conducting material, such as a metal foil or sheet, or paper loaded with carbon black. It is preferable that the backing sheet have a lower resistivity than the coating.

Any colored photoconductor having a sufficiently high value of surface conductivity may be used. For example, the colored oxides, sulphides, selenides, tellurides and iodides of cadmium, mercury, antimony, bismuth, thallium, indium, molybdenum, aluminum, lead, and zinc. In addition, arsenic trisulphide, cadmium arsenide, lead chromate, and selenium may be used. It is preferable for the photoconductor to have a high resistivity in the dark. Mixtures of one or more photoconductors may be used.

The photoconductive material will determine the spectral response of the printing base since it is the photoconductive material which converts the light image to an electrostatic image. The color of the photoconductor indicates approximately the location of the absorption edge of the photoconductor and the printing base. Most photoconductive materials absorb light in the shorter wavelengths. As the wavelength becomes longer, a point is reached where the absorption drops off sharply and the photoconductor ceases to absorb the radiation. This point is called the absorption edge of the material. It is of particular advantage, in the present invention, that by making a proper selection of the photoconductor one may obtain a printing base with any desired light absorption characteristics and therefore desired spectral sensitivity. For example, thallium iodide has a peak response around 4130 Å., silver sulphide has a peak response around 13500 Å. while other photoconductors may have their peak responses at other points of the electromagnetic spectrum and over a narrow or wide band of frequencies.

The electrically-insulating, film-forming material is an essential part of the composition. This vehicle may preferably be any one of a number of substances. Most desirable is a film-forming material having a relatively high dielectric constant and high dielectric strength. These materials may be natural or synthetic resins or waxes. Examples of suitable resins are the vinyl resins, silicone resins, phenolformaldehyde compounds and cellulose ethers and cellulose esters. Shellac is an example of a suitable natural resin. Examples of suitable waxes are paraffin, carnauba wax and beeswax.

The photoconductive material may be suspended in the vehicle in any of several ways. The simplest way is to dissolve the film-forming material in an organic solvent capable of effecting solution and then mixing in the powdered photoconductor. Alternatively, the photoconductor may be dry-blended by kneading with the film-forming ingredient heated to a sufficiently high temperature to render it plastic. In the case of the waxes, they may be melted and the photoconductor mixed with the melt.

The proportion of powdered photoconductor to film-forming material in the final coating may vary over a very wide range. The preferred ranges are 50% to 90% of photoconductor and 50% to 10% of film-forming material. The optimum proportions will depend upon the nature of the photoconductor, the film-forming material and the results desired.

The speed of response of the printing base is partly dependent upon the nature of the photoconductive material, the nature of the film-forming material and the ratio by weight of photoconductive material to film-forming material. Since the speed of response depends on a balance of characteristics of these factors, almost any desired response may be obtained by proper selection of materials and compositions.

A proper selection of materials and compositions will also determine how long an electrostatic image may be stored, since storage of the electrostatic image depends

upon the resistivity of the coating. Generally, the higher the resistivity of the coating the longer the storage time.

A coated or impregnated and dried paper, prepared as above described, comprising a printing base may be utilized as follows to receive an image thereon. Referring to Figure 1, according to the invention, an electrostatic charging device 13 is passed, in darkness, over one of the coated surfaces 12 of a printing base 11 to provide an electrostatic charge thereon. The charging device may comprise an array of fine wires 14 mounted near a grounded metal plate 15. A source of D.-C. high voltage (not shown) is connected between the wires and plate to provide a negative charge on the wires with respect to the ground plate. The voltage should be sufficiently high to cause a corona discharge adjacent the wires. The printing base 11 is placed in contact with the ground plate and passed through the corona discharge and thus becomes charged negatively. The same apparatus and process may be used to give a blanket positive charge if the leads are reversed. The apparatus shown in Figure 1 may require enclosure in a light-tight box or a room with a suitable safety light depending on the sensitivity of the printing base 11.

The next step in the process is to discharge selected parts of the charged surface of the printing base in order to provide an electrostatic image thereon. Referring to Figure 2, this may be accomplished by removing the printing base from contact with the grounded plate 15 and exposing it to a desired light image derived, for example, from a sheet 17 containing printed matter 18. The light image is focused on the charged surface 12a with the aid of an optical system 19, using light from one or more incandescent bulbs 20. The sheet containing the material to be copied is placed in one compartment A of a light-tight box and the sheet which is to receive the print may be placed in another separate compartment B of the box. The subject to be printed may, however, be any subject used in ordinary photographic processes for example, natural surroundings and interiors, or projections from images on a photographic film. The light image may also be projected by scanning a group of letters, characters, and figures in the form of a stencil, with a light spot from a cathode ray tube, or the spot from the cathode ray tube may be merely scanned across the charged surface 12a in response to an electrical signal received from an external source. Similarly, any type of electromagnetic radiation may be used depending on the spectral sensitivity of the coated surface. For example, visible light, infra red, and ultra violet rays.

Wherever the light strikes the charged coating layer 12a, the electrostatic charge is reduced or removed. This leaves an electrostatic image or pattern of remaining charges 21 corresponding to the dark portions 22 of the light image.

The electrostatic image may be stored for a time, if desired. Ordinarily, however, the next step in the process is to develop the electrostatic image to render it visible. This may be accomplished by maintaining the sheet in a darkened condition and, as shown in Figure 4, dusting the charge image 21 with an electroscopic developer powder 23. When a low-sensitivity coating is used such as described in Example 2, the electrostatic image may be developed in ordinary room light.

A suitable developer powder is disclosed and claimed in the copending application of H. G. Greig, Serial No. 187,827, filed September 30, 1950. A developer powder of this type may be prepared as follows: Mix 40 parts by weight of sublimed sulfur with 50 parts by weight methanol to form a thin slurry or paste. Mix 1.5 parts by weight of spirit-soluble nigrosine dye SSB, Color Index No. 864 with the paste until the dye is completely dissolved in the methanol. Then add 1 part by weight of Iosol Black, or any other dye which will react with the nigrosine, to precipitate a black dye. The product is filtered, washed with a small amount of methanol and dried. This powder can either be used as is, or after

grinding in a ball mill to enhance its electroscopic properties.

Instead of merely dusting, the powder may be applied to the image by mixing with small glass beads or other suitable carrier particles and then bringing the mixture into contact with the surface of the paper. The beads serve merely as a temporary carrier for the powder.

The type of powder above described is a positively charged powder and will readily adhere to negatively charged areas of an electrostatic image. The developed image 24 obtained using the precipitated dye-treated sulfur powder described above is a positive, that is, the dark portions of the developed image correspond to the dark portions of the original. Alternatively, the printing base may be charged positively. If the same steps are carried through as above described, a negative is obtained. If negatively charged powders are used, then a negative is obtained in the first case and a positive is obtained in the alternative case.

The developed image 14 on the printing base may be fixed so that it does not smear in handling. If the developer powder or vehicle has a base of low melting point, the image can be fixed by heating, for example, with an infra-red lamp, to fuse the powder to the surface. The dyed sulfur or dyed synthetic resin powders can be fixed in this way. The developed image may be fixed by spraying with a lacquer or with shellac if the powder is not fusible at relatively low temperatures.

The process of the present invention, as above-described, has a number of advantages compared to the type of process employing a selenium plate. After the charging step, the printing base can be removed from the ground plate for exposure and developing. A visible image can be placed directly on a printing base comprising a sheet of material such as paper, with no conductive backing required. It is also apparent that the coating compositions used as a necessary part of the present process have certain advantages not possessed by previously used materials, such as white zinc oxide or selenium which result in improvements in the process of the present invention.

As in the previously referred to process of H. G. Greig described in application Serial No. 248,937 and now embodied in continuation-in-part application Serial No. 383,677, filed October 1, 1953, the coated paper can be prepared in roll form and can therefore be used in a continuous printing process. For example, the sensitized paper may be unrolled and conducted along a predetermined path where it is given a charge, and then exposed to a series of light images either as the paper passes a certain station or a plurality of stations. As the paper continues to travel, the developing powder may be applied to the exposed surface such that a series of images are developed, and then the developed images may be fixed.

The present invention has the further advantage that one may select a printing base having a desired speed of response, spectral response and contrast characteristic for the image to be printed. This makes possible obtaining optimum prints in many fields of photography and duplicating. The printing base of this invention may be adapted to take a positive or a negative blanket charge and positively or negatively charged electroscopic powders may be used to develop a positive or a negative final image.

What is claimed is:

1. A process of printing which comprises providing a backing sheet having a surface coated with a composition comprising about 50% to about 90% by weight of lead iodide suspended in an electrically-insulating, film-forming, resinous, organic binder selected from the class consisting of polystyrene, silicone, phenoformaldehyde, cellulose ether and cellulose ester, said organic binder correspondingly comprising 50% to 10% by weight of said composition, said surface coating having a volume resistivity greater than said backing sheet, forming an electrostatic image on said coated surface, applying an elec-

troscopic powder to said electrostatic image to render it visible and fixing said image to said coated surface.

2. A process according to claim 1 wherein said backing sheet is paper.

3. A process according to claim 1 wherein said backing is paper and said vehicle is a silicone resin.

4. A printing base comprising a backing sheet having a surface coated with a mixture comprising about 50% to 90% by weight of lead iodide suspended in an electrically-insulating, film-forming, resinous, organic binder selected from the class consisting of polystyrene, silicone, phenol-formaldehyde, cellulose ether and cellulose ester, said organic binder correspondingly comprising 50% to 10% by weight of said mixture and said surface coating having a volume resistivity greater than said backing sheet.

5. A printing base according to claim 4 wherein said vehicle is a silicone resin.

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