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ELECTROPHOTOGRAPHIC REFLEX AND CONTACT PRINTING

Filed Dec. 22, 1958

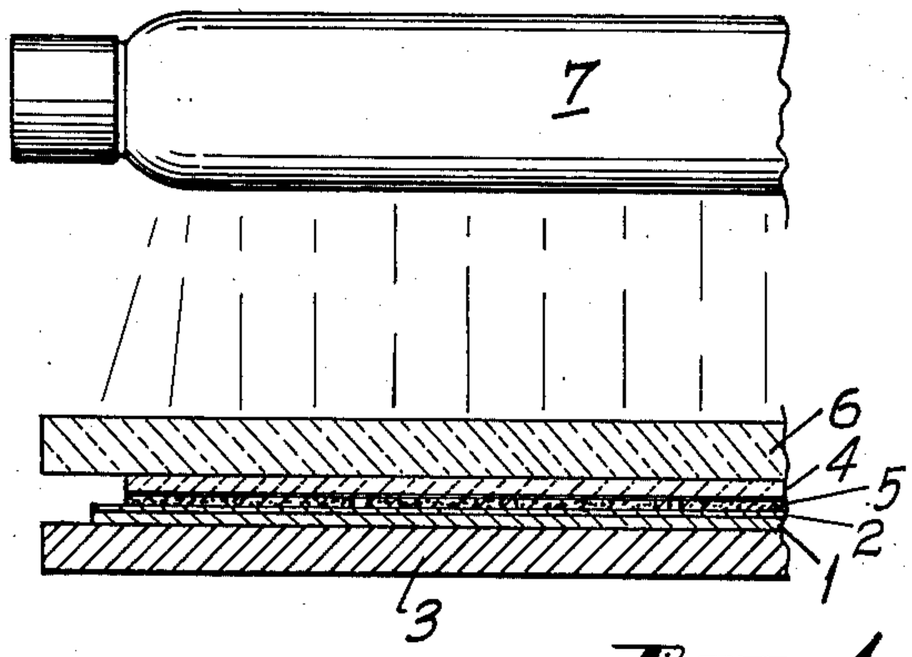

FIG. 1

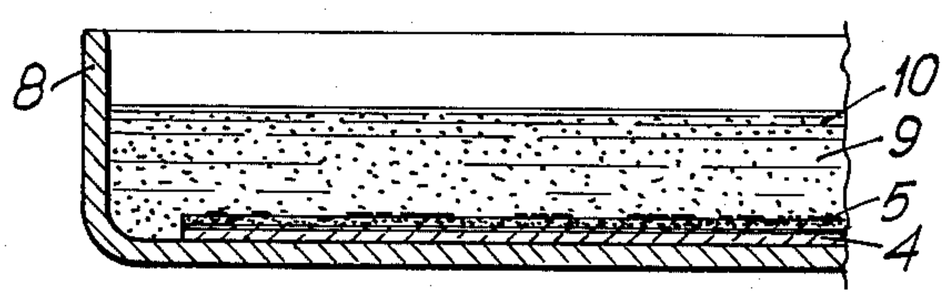

FIG. 2

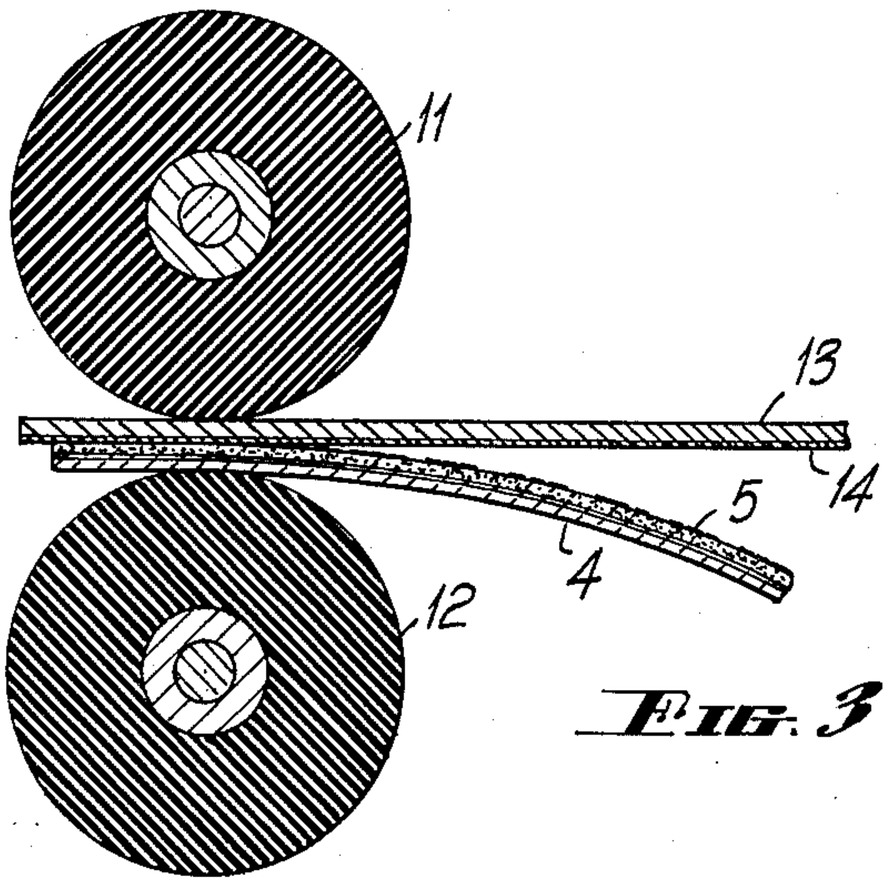

FIG. 3

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ELECTROPHOTOGRAPHIC REFLEX AND CONTACT PRINTING

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1 Claim. (Cl. 96—1)

This invention relates to electrostatic reflex and contact printing and more particularly it relates to a method of producing printed matter and the like by direct means without the use of lenses.

By electrostatic printing is meant generally producing an image, reproduction, or copy, by including a step in which a light image, electrostatic image, X-ray image or scanned image or pattern is used to control the leakage of an electrostatic charge from the surface of a photoconductor layer or insulator layer in such a way as to produce a latent electrical image or pattern on the surface of this layer. The latent image is then developed or made visible by exposing it to an environment in which there is dispersed an electroscopic powder or medium which adheres to those portions of the pattern where a charge remains after the exposure to light or the like.

The electrophotographic surface may comprise any layer of photoconductive insulating materials such as amorphous selenium, zinc oxide, linseed oil boiled with sulphur, phosphors or the like. The material can be used in the form of thin layers, pressed powders or in other suitable forms.

The material to be copied may be reproduced by a contact printing process in which the original is placed adjacent to the photo-electric layer and illuminated so as to throw the shadow of the printing or drawing onto the photo-electric layer either by reflexing or by direct passage of the light through the paper or the like.

This method has the advantage of requiring no lenses which cut off part of the ultra-violet spectrum and, hence, photo-electric materials which are sensitive mainly to the shorter ultra-violet waves can be used.

A feature of the invention is the use of thin layers, such as in the order of a 1.5 to 20 microns for selenium to 100 microns for zinc oxide. The layers may be continuous or discontinuous in nature or, in other words, the layers may be made up of a plurality of discrete tiny individual areas of photoconductive insulating material, or the material may be made up into a more or less porous layer.

Where the original is a transparency or translucency such as an ordinary photographic film, or a translucent material such as ordinary paper carrying an image in the form of opaque or semi-opaque lines or areas, the original, carrying the image, may be placed against the surface of the photoconductive layer after said layer is charged electrostatically and the assembly exposed to light from a suitable light source. Exposure of from a fraction of a second to a few seconds will ordinarily suffice. Ordinary drawings and typewritten letters may be copied in this way.

Development of electrostatic images is by the liquid development technique developed by applicants, which produces a fine grained image suitable for high resolution work, particularly on the amorphous films and layers such as selenium and sulphur. The invention has particular relation to the liquid development disclosed in Australian patent specification No. 24,202/56.

In the reflex printing field, the invention contemplates forming the image electrostatically by means of back reflection printing in which light is passed through the back of the charged electrophotographic layer to be reflected back by the original to be copied so that the letters and other matter on the original produce more or less back reflected light according to their density and color. The invention further contemplates the use of transparent or translucent layers of photoconductive material as the photoconductive layer and the said layer may in this case be any of the aforementioned materials but preferably such materials as amorphous selenium and also a layer of a photoconductive material such as zinc oxide, lead iodide or the like dispersed in a resin insulator matrix.

In the practice of the present invention excellent results have also been achieved with zinc oxide-impregthickness below about 20 microns, but it is found that the best results are obtained in electrophotography with selenium if layers of the order of 1.5 microns are employed, these having the advantage that they are transparent and the transparency may be improved after development by dissolving away the selenium from the non-image areas after development which leaves a clear background. The dissolving medium used is carbon bissulphide which is effective on thin layers. A red light should be used in exposure due to the red color of the selenium.

In the practice of the present invention excellent results have also been achieved with zinc oxide—impregnated resin layers having a thickness of 100 microns. White zinc oxide has a sensitivity to radiation greatest in the range 2900 to 3900 Angstrom units which requires ultra-violet light for best results. Other photoconductive materials have a more appropriate response in the visible portion of the spectrum but usually they are colored substances and therefore are not desired where the image is to be fixed to the original surface which should be white.

Also in the practice of the present invention it has been found that the film of amorphous selenium should preferably be thin such as only 1½ microns if it is desired to avoid the production of artefacts which are common in the production of thick films of selenium.

Further it is possible that with the cruder forms of development that the artefacts are not noticed but are only seen in their correct perspective when liquid developers are used, these developers allowing much greater resolution. It has been found that the low voltages which can be built up on the thin films can be used to advantage in electrophotography only if the liquid developers are used and preferably only if triggered developers are used in which a much greater yield of material is possible for a given charge on the plate.

Accordingly the present invention envisages the use of thin films of selenium or of zinc oxide and the like in an insulator matrix the latter having a spectral response more appropriate to the application conferred on it by the addition of sensitizing dyes such as rose bengal, eosin, erythrosin and the like which extend the sensitivity and the speed of response of the white zinc oxide coatings or alternatively the white dyes such as Tinapol which is added as a water solution to the zinc oxide to coat the surface and after which the zinc oxide is dried before being dispersed in a resin.

According to the present invention, for reflex printing, the layer is formed on glass, film base or the like or thin paper with good transmission of light. After charging to give it a blanket electrostatic charge the layer is placed face down on top of the original to be copied and the assembly is then held tightly in juxtaposition by means of a glass plate or the like and the assembly is then exposed

to light through the back of the zinc oxide paper or the like. As said the light is differentially reflected back from the surface of the original so as to form an electrostatic image on the surface of the photoconductive layer. The base with the layer therein is then removed and developed to bring up the solid visible image which is of course a mirror image of the original image.

Before the liquid developed image is dry, and preferably just after development, the physical image is brought into contact with another sheet usually of paper which is of an absorbent or holding nature and the developed image is transferred to this second surface by bringing said second surface into close juxtaposition to the first surface and the image is transferred to the second surface which becomes the picture surface having a permanent character on a usual paper base. The first surface may be cleaned and subsequently re-used.

It is appropriate here to mention that in order to obtain a suitable surface on the zinc oxide-resin type layer it may be necessary to polish the surface after it has hardened or subject it to a pressurization operation in which the layer is compacted and a glossy surface is obtained. The residual images are more easily removed from this type of surface. There is of course little difficulty removing the residual material from the glassy selenium surfaces especially if they are carefully washed with acetone under the surface of the liquid. It may be desired in some cases to get the necessary gloss on the zinc oxide type of surface by coating it on a glass surface or the like in such a way as to make it removable after formation but before use as a layer because in this way it is possible within the scope of this invention to make a very satisfactory smooth film which meets the need for good contact between the layer and the original which must be pressed firmly in contact during exposure, in order to avoid diffusion of the back reflected light.

To enable the invention to be fully understood, embodiments thereof will now be described, with reference to the accompanying drawings in which:

FIG. 1 is an enlarged sectional fragmentary view of an assembly in reflex printing, showing the exposure stage,

FIG. 2 is a fragmentary view of the developer stage, and

FIG. 3 is a fragmentary view showing the transfer stage.

In FIG. 1 the original **1** to be copied is placed with the image **2** or the like face up on a base board **3**. On top of this original **1** there is placed the charged photoconductor sheet **4** having its active surface layer **5** in contact with the image. To press the layers in contact a sheet of glass **6** is used. The assembly is then exposed to light from the light source **7** placed at a suitable distance from it so as to give good sharpness and at the same time a reasonable exposure time.

Having made the exposure the photoconductor sheet **4** is placed in the developing dish **8** or the like (see FIG. 2) in which is contained the developer liquid **9** which itself contains the developer particles **10** which are caused to be attracted to the charged areas of the image and to form a solid visible image on the surface of the photoconductive layer **5**.

The photoconductor sheet **4** is then removed to the transfer station (see FIG. 3) which comprises the rollers **11** and **12** and is passed through between the rollers in close juxtaposition with a transfer paper **13**, this paper having a thin layer **14** of glue or the like on it. The assembly is passed through the rollers which are under pressure and the image transfers to the paper **13**.

To fully understand the invention, the following examples are given.

Example of Production of a Selenium Plate

In the case of selenium, the selenium is heated in a small furnace, to its evaporation temperature, which is about 250° C., when a vacuum of the order of 10^4 millimeters of mercury has been achieved. This is done in a chamber either of glass or metal which is suitably tabulated by valves and fittings to an oil diffusion pump backed by a mechanical vacuum pump. The plate on to which the selenium is evaporated is maintained at ambient temperature or is cooled in some way. The thickness of the selenium film is between 1.5 and 20 microns, at which the film is relatively transparent but of a reddish color.

Provision for ionic cleaning in the vacuum chamber, however, ensures that absolute cleanliness can be obtained before the selenium is evaporated. Any traces of absorbed moisture or a monomolecular organic layer are removed by ionic cleaning the result of which is a perfect bond between selenium and glass of light transmitting substrate.

The ionic bombardment which produces this effect is done in the roughing pump down stage when sufficient air remains in the chamber or is bled into the system giving the desired electrical condition for applying the high voltage current to the aluminium rings within the chamber.

Immediately after ionic cleaning, but before any contamination can condense on the plates, the chamber is further evacuated to a pressure of 10^4 millimeters of mercury by the diffusion pumping system. The removal of the gas molecules ensures that the evaporating selenium will have unimpeded paths to the cooled base plate.

The substrate is preferably glass to which a transparent film of cadmium oxide has been sputtered which also inhibits the crystallization of amorphous selenium because of the stoichiometric excess of cadmium metal in the oxide film.

This sputtering process also ionically cleans the glass rendering it in a condition immediately ready for the selenium evaporation.

There is quite a range of temperatures at which selenium plates can be made but refrigerated water at say 5° C. is preferably circulating through the platen on which the base plate is attached.

The selenium plates are made completely in the dark.

Although the selenium plates can be used many times, great care in handling them should be exercised. The surface of the selenium should not be touched with the fingers and the image developed by liquid developers can be removed, as can dust which is attracted to the selenium plate after charging, by immersing the whole plate into a shallow bath of acetone and using gentle action of a squirrel hair brush under the liquid until the image and dust particles are removed. Such recovery treatment will give the plate very long life.

Examples of Production of a Zinc Oxide Photoconductor

(1)

80 grams of a silicone resin 60% solids,
105 grams of toluene,
130 grams of white zinc oxide, indirect process, non-fluorescent.

A solution of 0.04 gram of the dye rose bengal in 5 cc. of methyl alcohol was also prepared and this solution was added slowly to the above mixture with constant stirring. The mix was then ball-milled in a ball-mill with porcelain balls for about 18 hours to ensure complete mixing of the ingredients and to obtain the essential smooth uniform consistency necessary. The medium so prepared was then diluted with 50% by volume of toluene and electrocoated on to an art paper about 0.0005 inch thick, to produce a very uniform layer.

This paper then becomes the base paper or reflex printing after buffing the surface with a buffing wheel coated with lamb's wool or by passing it between rollers pressed together at a pressure of 700 lb. per foot length or roller, which gives a smooth glossy surface.

(2)

	Grams
"Rhodene L9/50" alkyd resin	80
Toluene	100
Zinc oxide paint pigment	200
Cobalt naphthenate	0.5
Manganese naphthenate	0.5

("Rhodene L9/50" is the trade name of an oxidizing type of linseed oil modified alkyd resin, oil length 40%, acid value 25–35, specific gravity at 20%, 0.98–.099.)

This liquid is ball-milled for 18 hours and then applied to the surface of a base paper or the like having a translucent or transparent nature such as tracing paper, film base or the like, by electro-coating means to give the surface the necessary smoothness and uniformity following which it is smoothed off by a pressurization or buffing operation already referred to.

Examples of Developers

(1) A developer paste is prepared as follows: a mixture comprising 100 grams of aluminium powder mixed with an organic solvent such as mineral turpentine or toluene is dispersed by ball-milling in a varnish base for instance 100 grams of "Rhodene L26/50," a dehydrated castor oil modified alkyd resin of medium oil length, dispersed in 100 grams of solvent such as toluene. The individual particles of this paste take on a positive charge when suspended in a liquid of high volume resistivity and low dielectric constant such as cyclohexane or carbon tetrachloride. It therefore develops an electrostatic image composed of negative charges in a photographically positive manner. When an image developed in this developer is transferred to the image receiving paper from the photoconductor layer, a positive image of the original results. Other powders which may be made up in this way include the following: powdered zinc, powdered copper, carbon, sulphur, natural and synthetic resins and mixtures thereof.

(2) A developer may be formulated in the following manner:

	Parts by weight
"Pentarol 20" resin	15
"Rhodene L6/100" resin	15
Solvent, xylene	25
Pigment, carbon black	60

("Pentarol 20" is the trade name of a phenol modified penta-erythritol ester of rosin, acid value 7–15, specific gravity at 20° C. of 1.09. "Rhodene L6/100" is the trade name of a linseed oil modified alkyd resin of medium oil length, acid value 6–10, specific gravity at 20° C., 0.955 to 0.965.)

This paste is prepared as follows: the Pentarol 20 is digested in xylene by heating the mixture until the resin is dissolved in the solvent and the Rhodene L6/100 is then stirred in to make what we call a developer base. Allowing for the evaporation of the solvent during the digesting operation, the above quantities will make about 50 grams of developer base. The pigment is then mixed with the resins and blended until mixing is complete and the particle size has been reduced to the desired fineness. As this forms a viscous paste it will be necessary to use a triple roll mill or an ultra sonic mixer for this blending operation. The normal colors for color printing are red, yellow, blue, black. Obviously developers of other colors may be made by mixing the necessary primary colors either in paste form or as developer suspensions.

(3) A developer may be formulated in the following manner: 20 parts of a rosin-modified alcohol soluble cresylic resin designed for use in spirit varnishes and hard drying gloss varnishes such as that known by the trade name "Caladene 5H" marketed by the Polymer Corporation, melting range 105–115° C. and 1 part of carbon black are ground together with mineral turpentine to form a cream which is then dispersed in mineral turpentine together with cyclohexane in the proportion 95 parts to 5 parts by volume.

Example of Transfer Receiving Base

The transfer paper may be any ordinary paper filled or unfilled which when passed in contact with the wet image on the photoconductive surface will absorb and take off the developed image. To improve the transfer it may be desirable to treat the paper with a solution of glue, gum or the like beforehand to increase the adhesive properties and lessen the pressure necessary to effect the transfer. Materials suitable include gums such as arabic, mesquite, karaya, locust bean, guar, ammonium alginate and sodium alginate. Proteins such as casein, soya bean protein, zein, animal glue, gelatin, albumin. Others include synthetics such as carboxy methyl cellulose, sodium polyacrylate, methyl cellulose, hydroxy ethyl cellulose, polyvinyl alcohol and the like. Others include starch, dextrin, pectins and various derivatives of these and latex derivatives. Others include the synthetic resins such as Rhodene alkyd resins, Caladene resins and the like which may be wetted with solvent just prior to transfer to bring about an adhesive condition. Other suitable materials are available in the form of pressure sensitive tapes.

Art paper with a smooth surface on one or both sides with or without an added adhesive such as animal glue in small proportion may be used, and the wetting agent may be water, but wax, paraffin or other soft or sticky substances may also be used. Where the developed image comprises a substance which is soluble or partly soluble in water or other liquid and the liquid is used to wet the paper or other transfer material prior to transfer of the image, the image will become enhanced and permanent on the sheet as soon as the liquid evaporates, thus resulting in a finished copy.

Where a wax or sticky material is used the developed image may in some cases be sufficiently embedded by pressure to produce an acceptably permanent image.

Accordingly an example is an ordinary paper or piece of hardboard or the like soaked with a liquid such as water or alcohol which is brought into contact with the image which is itself soluble in the liquid such as a water soluble dye or such dyes as are used in hectograph production such as rhodamine, victoria blue, nigrosine, methyl violet and the like.

Charging of Photoconductor Surface

In order to carry out the invention it is necessary to charge the paper or plate and this is done by passing the photoconductive assembly through a device in which there is an array of points such as needle points held at a high potential above a base plate of metal or other conductive material the potential being of the order of 10,000 volts per inch. After charging the paper or transparent backed photoconductive layer is placed face down on the original to be copied and light is passed through from the back of the layer that is opposite to the original. The exposures may be for example as follows:

(1) White zinc oxide coated on plain white art paper exposed to light from a 150 watt blue actinic lamp at a distance of 2 feet for 30 seconds, to copy printed matter on art paper.

(2) Zinc oxide paper activated with rose bengal coated on white art paper under conditions as above, requires a shorter exposure of 3 seconds.

(3) A thin selenum film of thickness 1½ microns on a glass backing with a cadmium oxide substrate requires an exposure under generally similar conditions of 30 seconds with red filtered light.

It will be appreciated that in an apparatus designed for continuous operation that the exposure will be in terms of slit opening and light source wattage for a given speed of operation, and that the transfer to the paper or the like will be continuous and will of course occur before the liquid from the liquid develper has evaporated from the image in which case transfer is

rapidly and accurately effected, with a minimum of adhesive on the transfer paper or none at all.

In the specification and claims "light" is intended to refer not only to visible radiation but also to other radiations which affect the photoconductive layer such as ultra-violet radiations, infra-red radiation and the like.

We claim:

A method of making a xerographic reflex copy from a master which comprises applying a film of cadmium oxide to a light transmitting substrate to form a conductive backing, applying a uniform layer of selenium thin enough to be translucent and about 1.5 microns to said conductive backing, electrostatically charging the surface of the said layer, exposing the said master to light through the said selenium and backing with the latter in contact with the said master to render areas which are light-struck more conductive than the other areas whereby to bleed away the charge selctively to form an image, developing the image with a liquid developer comprising a pigment which has been precoated with a control and fixing agent and suspended in a carrier liquid having an

electrical resistivity of at least about 10^{10} ohm-centimeter and a dielectric constant less than 3, and transferring the image so developed while wet to a transfer-receiving base.

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