June 23, 1964 D. G. KIMBLE ET AL 3,138,458

ELECTROPHOTOGRAPHY

Filed Sept. 30, 1955

FIG. 1

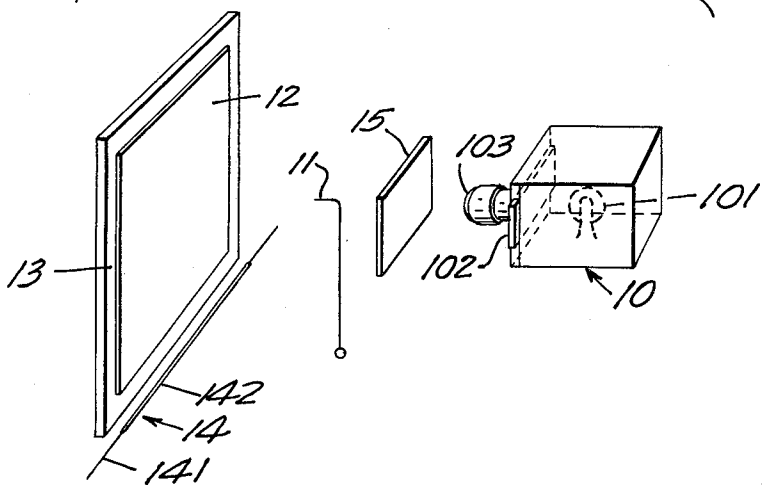


FIG. 2

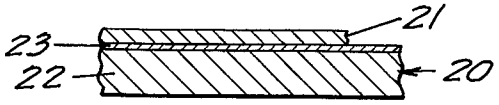


FIG. 3

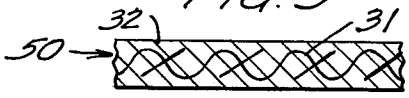


FIG. 4

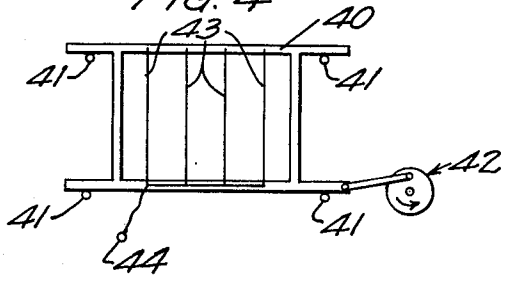
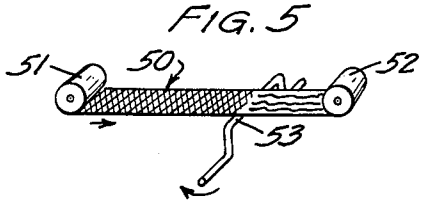


FIG. 5



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ELECTROPHOTOGRAPHY

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This invention is primarily concerned with the printing or permanentizing of light-images, optically produced in accordance with well-known principles employed in photography or photo-copying, by a dynamic electrophotographic process employing copying-paper or the like having a photoelectrosensitive surface. The process involves establishing a high potential difference between the copy-paper and a corona electrode while the sheet is under the influence of a light-image, and then passing an aerosol developing agent across the face of the sheet while maintaining a high potential at the sheet or the electrode or both. The invention concerns the copy-sheet and the equipment and apparatus employed, as well as the novel dynamic copying-process.

Accordingly, one of the objects of the invention is the provision of novel and useful methods and processes for the printing of light-images. Another object is the provision of apparatus suitable for carrying out the novel processes. A further object is the provision of materials for use in conjunction with said apparatus in producing visible copies of light-images by said methods. A still further object is the provision of copy-sheet material adapted to the preparation of permanent, smudge-resistant copies of impressed light-images, including multi-color images, by methods here described. A specific object in the dynamic development on such copy-sheets of both direct and reverse visible copies having extremely high contrast, by methods involving continuous or intermittent deposition of any desired amount of the developer material. Other specific objects are the provision of methods for the printing of light-images under adverse humidity conditions; in a continuous rapid manner, e.g., by simultaneous exposure and development; and with the production of continuous-tone images and of uniform density solid image areas. A still further object is the provision of methods permitting the production of visible images on poorly insulative photoelectrosensitive sheet materials and with a wide variety of developer materials including both readily charged and difficultly charged developer materials. Another object is to produce prints having high resolution and freedom from smudging, and by simplified and rapid procedures.

The present invention accomplishes there and other objects and provides numerous advantages, as will be made apparent or will be specifically pointed out hereinafter.

In the accompanying drawing:

FIGURE 1 illustrates in perspective, and largely schematically, the minimum requirements of the apparatus of the invention;

FIGURE 2 illustrates in cross-section a preferred type of copying-paper employed in the process of the invention;

FIGURE 3 illustrates in cross-section a preferred source of image-producing components; and

FIGURES 4 and 5 schematically illustrate details of

alternative structure employed in the apparatus of FIGURE 1.

The apparatus depicted in FIGURE 1 comprises an image source **10** from which the image is projected, through a filter **15**, if desired, past a corona source **11** and against a suitable receptor **12**, in this instance a flexible copying-paper held in contact with a conductive support **13**. A high voltage direct current power supply is connected between the corona source **11** and the support **13** or the receptor sheet **12**. An element **14** providing a source of image-producing developer components is located adjacent the lower front surface of the copy-sheet **12**.

A light-image is projected on the receptor **12** from the projector **10**, a suitable image-producing developer component is released from the source **14** in the form of an aerosol, i.e., a cloud of extremely fine particles suspended in the air, and a suitable high potential difference is established between the plate **13** and the corona source element **11**. The combination of the light-image on the receptor **12** and the high potential difference between the plate and the point source **11** causes particles to be preferentially and continuously transposed from the aerosol to image areas of the receptor, where they are deposited and retained to form a copy of the initially applied light-image. Where contrasting dye or color particles form the image-producing developer component, the copy produced is directly visible.

It has been found that the process just described is capable of producing completed prints within surprisingly short periods of time. The prints are of exceptional clarity, showing the finest detail which it has been possible to project by high quality optical systems. Permanent prints may be made directly, without any need for subsequent fixing or processing. Depending on the character of the components employed, the print may be made in any desired color or combination of colors, including black and white. Printed areas, such as line or block areas, are uniformly colored over their entire area rather than being intensified along edge areas as in many electrical printing processes. Printing may be continued to any desired thickness of the developer material. Prints capable of serving as master copies or as printing-plates, for subsequent reproduction by well known duplicating methods such as dye transfer or lithography, are easily made.

It is to be understood that each of the several components of the apparatus indicated in FIGURE 1 may be replaced by any of a variety of equivalent components providing equivalent functions and operating on the same principles. Further elaboration of these principles will now be provided.

The projector **10** of FIGURE 1 includes a source of light **101**, a transparency **102** carrying the graphic subject-matter and through which the light is directed, and a lens system **103** for focusing the resulting modified light beam on the surface of the receptor **12**. Such devices are in common use as slide projectors and for photo enlarging. A sharp image of high contrast is provided. The intensity and duration of exposure is easily controlled. Analogous systems reflect the image from an opaque print, as in photocopying, or transmit an image from a lighted subject, as in photography. These and other optical systems may replace the projector **10** of FIGURE 1, provided sufficient space is made available adjacent the irradi-

ated surface for establishing an effective corona and for uniformly introducing and distributing the image-producing aerosol. It will be apparent that excessive extraneous light must be eliminated in order to provide the required image pattern and intensity at the surface of the receptor.

The term "light" as applied to the radiation provided from the projector **10** will be understood to include monochromatic light and various invisible radiations as well as the white light ordinarily employed for image projection. Infra-red radiations have been found useful in some instances. Ultraviolet light, in the neighborhood of 3600 Angstroms wave length, has proven particularly suitable; and radiations of still higher frequency, such as X-rays and radiations from radioactive sources, are also useful under specifically somewhat different but analogous conditions. In the latter case, shadow-graph processes are conveniently employed, involving irradiation of the sensitive surface through a suitable stencil held at a distance from the surface sufficient to provide space for the corona source and the aerosol developer. In all cases, the radiation used must be capable of producing the required differential effect at the receptor surface.

Multi-colored prints are formed with ease and rapidity by the process of the invention, employing colored transparencies such as "Kodacolor" negative slides to establish the light-image, and passing the light through the proper color-filters in succession while providing a corresponding succession of colored aerosols from source **14**. One such color-filter is indicated in FIGURE 1 by the filter **15**; it will be apparent that such filters may equally effectively be placed between the light source **101** and the transparency **102**. These filters are omitted where color separation or intensification is not required.

It is to be understood that the term "print" refers to the visible or other image formed at the receptor surface by selective deposition of aerosol developer particles, whether in the form of an immediately visible deposit of ink or dye or the like, or as an invisible deposit of material which is self-reactive or visibly reactive with components of the receptor or with reactants from other sources and is subsequently to be converted to visible form, or as an adherent coating for retaining subsequently applied powders, inks, or other materials, or as transparentizing means for the receptor sheet, or in any other analogous form. Pictures or photographs, made either directly from the subject or from orginal negatives or positives, as well as reproductions of printed matter or drawings, are examples of prints which may be made by the methods and with the materials and apparatus of this invention.

The corona source **11** is illustrated as a single point and is supplied with high voltage from a suitable source, not shown. The single point source is the most effective in setting up the required conditions, but must be separated from the sensitive sheet by a distance equal to at least approximately the diagonal of such sheet if a uniform image is desired. Hence the use of a single point source is practical only for small areas. Increasing the number of such sources requires additional current and has the further disadvantage, in many instances, of forming "zones" in the print. The latter difficulty is experienced also with some line sources of corona. Since line source or multiple-print source systems permit the printing of much larger areas and at much greater speeds, it is desirable to substitute them for the single-point source. It has been found that such substitution is effective if the point or line sources are carefully properly spaced from each other and from the sheet, or, alternatively, if they are caused to oscillate parallel to the surface of the receptor. Either of these procedures is found to make available substantially uniform distribution of the aerosol developer particles over the entire receptor surface. A specific example of a suitable non-oscillating grid system employs a series of No. 36 B & S gauge fine parallel wires spaced at ½ inch from each other and at one inch from the receptor surface. The system produces a substantially

shadow-free and zone-free print at a potential difference between the grid and the plate of 20,000 volts.

An oscillating multiple corona source is represented in FIGURE 4. A frame **40** is moved alternately in both lateral directions on rollers **41** by means of a crank mechanism **42**. The frame **40** carries a plurality of parallel line corona source elements **43** which are connected to a source of potential, not shown, through connector **44**. A series of spaced point sources, or a single line source, or a coarse screen having crossed line sources and oscillating in both the vertical and the horizontal directions, may replace the line source elements **43**. The device replaces the single point source element **11** of FIGURE 1 and is advantageously placed much closer to the receptor **12** than is possible with the point source, thereby lowering the required voltage and reducing the space requirements.

The relatively high charging current requirements of the device illustrated in FIGURE 4 may be reduced by mechanically distributing the input potential to each of the several corona sources independently and in sequence. Such an arrangement reduces the zoning, and eliminates the need for accurate spacing, previously referred to.

Various volatilizable dyestuffs have been found to be well adapted to the requirements of the process of this invention. In order to obtain the desired high speed of printing, it is necessary that the aerosol formed of these or other materials be introduced into the space between the receptor and the source of corona without delay and with maximum uniformity. Furthermore the individual particles of the aerosol must be extremely small in order to obtain adequate definition in the print; and smudge resistance is also improved. The present invention provides rapid controllable formation and uniform distribution of aerosols having extremely fine particles by substantially instantaneously volatilizing the dyestuff or other active developer material from an inert carrier and with substantially no decomposition. Introducing the resulting aerosol into the desired space is readily accomplished by controlled convection in the apparatus illustrated in FIGURE 1.

In the apparatus of FIGURE 1, the aerosol of suspended developer particles is produced at source **14** by electrically heating a section of wire **141** coated with a thin layer **142** of the developer material. The cloud of aerosol rises by convection in front of the face of the sheet **12**. The wire **141** with its coating **142** may be continuous, being drawn past the indicated position and electrically activated along the portion indicated through suitable clamp means, not shown. The rate of heating is sufficiently rapid to produce complete volatilization of the dyestuff or other developer material without any substantial decomposition.

FIGURE 5 illustrates another and preferred way in which an aerosol of a developer material may be produced. A belt **50** is drawn from a supply roll **51** to a windup roll **52** as needed, by mechanism not shown. The belt passes the path of a rotatable electrically heated crank member **53**. When a charge of aerosol is desired, the belt is drawn forward the necessary distance and the crank heated and revolved past and in brief wiping contact with the belt. The latter is initially impregnated with a developer material, in this instance a volatilizable dyestuff. Immediately on contact with the preheated crank surface, the dyestuff volatilizes to form the desired aerosol, which is then drawn across the face of the receptor. The intermittent contact action of crank and belt permits the former to reach full operating temperature before contacting the dyestuff, so that volatilization of the latter is practically instantaneous. The wiping action of crank on belt ensures a clean surface on the crank and full contact between the two surfaces. The operation may be made entirely automatic by the incorporation of available actuation and control means, not shown.

Moving the dye-impregnated belt over the surface of a hot wire or other heated body is also effective.

Rapid release of large volumes of extremely fine aerosols may be accomplished in other ways, e.g., by heating a dyestuff-impregnated belt or fabric with infra-red radiation. However, the automatic systems described above have a number of advantages and are preferred.

These methods produce aerosols of unaltered dyestuffs or other developer materials in which the individual particles are all extremely small and uniform, and in this respect differ from smokes, liquid sprays, and similar sources of air-dispersed fine particles. These latter materials contain many relatively large particles, and do not provide the resolution of image nor the permanency and smudge-resistant qualities such as are here made available. The extremely fine particle size of the aerosols produced may be illustrated by comparison of the settling rates in air of these and other fine particles. Glass tubes two inches in diameter and two feet in length were charged with equivalent densities of air-suspended extremely fine carbon black ("Darco" 5–51) and of aerosol produced by rapidly heating a resistance-wire coated with the dyestuff Alizarine Irisol N. The tubes were sealed and allowed to stand vertically. Most of the carbon black settled out within about 10 seconds, and the tube was found to be visually clear in 15 minutes. The aerosol, on the other hand, settled at a uniform and very much slower rate, and the tube was not visually clear until after 105 minutes of settling. Liberation of as little as 3 milligrams of dyestuff, or even somewhat smaller amount, is sufficient to develop a 7 x 7 inch print in apparatus as described in connection with FIGURE 1, again illustrating the extremely fine subdivision of the dye material.

The belt source of dyestuff or other volatilizable image-producing developer material is depicted in FIGURE 3 in cross-section, the belt **50** comprising an inert heat-resistant flexible fabric or fibrous base **31** impregnated and coated with solid volatilizable dyestuff **32**. Closely woven thin glass cloth is flexible, absorbent, and heat-resistant and is preferred as the base web.

Convection currents set up by the heating apparatus or by the heated aerosol of volatilized dyestuff are sufficient to move the mass of dispersed particles rapidly across the face of the receptor **12**, where the latter is properly protected and is not unduly large. Additional impetus may be provided, for example by a heating wire arranged across the top of the space through which the mass is to travel, where more effective movement is desired; or gentle air currents for transporting the mass may be set up by other means. For example, the aerosol source has been located in a duct somewhat removed from the edge of the sheet **12** the aerosol then being wafted through the duct and across the face of the sheet by means of a fan. Unused dyestuff may be recovered by filter action or by electrostatic precipitation in order to avoid venting the material to the surroundings.

The successful formation of prints by the method and with the apparatus hereinbefore described is dependent on the properties of the receptor **12**, which for convenience will in this description be referred to as the copy-sheet or copying-paper. A preferred copying-paper has a photoelectrosensitive powder dispersed in a binder film of low electrical conductivity which adherently bonds the powder particles to a flexible carrier sheet having comparatively high electrical conductivity. The structure is illustrated in FIGURE 2 in which a flexible conductive carrier sheet **20** is coated with a layer **21** of a mixture of sensitive powder and insulating binder. The sensitive layer may equally well be formed on relatively inflexible plates or other articles having a conductive surface, although for most uses the flexible carrier is preferred.

Useful papers have been produced in which the particles are incorporated within the sheet, as by addition to the pulp suspension, prior to paper formation of the dispersed particulate sensitive material usually in conjunction with small amounts of water-soluble or water-dispersed binder. The procedure is particularly attractive on an economic basis since subsequent coating and treating steps are eliminated and the sensitive paper is produced directly at the paper-making machine. Minor proportions of film-forming binder components are included in order to make possible the formation of a uniform and strong sheet with the required high proportion of particulate sensitive material, which should be present to the extent of at least about one-half the total weight of the dry sheet.

Sheet materials having a surface coating of the sensitive materials, while requiring additional handling, provide maximum contrast, are more generally applicable, and are preferred. In such cases, the particles of sensitive material are adherently affixed to a surface of the base sheet, e.g., by means of a film-forming organic binder material having high electrical resistivity. Preferred examples of suitable binder materials are polystyrene, chlorinated rubber, polyvinyl acetate, petroleum base diolefin resin, thermoplastic hydrocarbon resins, and polyamide resins.

Surprisingly, somewhat less electrically resistive binders may also be used, where development of the image is accomplished, as it is in the dynamic development processes of this invention, under a continuously maintained potential difference. Hence the process may be carried out under widely differing conditions of humidity etc. with no significant reduction in quality of the resulting prints.

In some cases the sensitive material may form the entire surface coating, being bonded to the surface of the sheet either by an intervening binder coat or by direct contact. Thus, selenium is useful in the form of a continuous film applied over the conductive base, for example by vapor deposition on a metal plate or foil. Anthracene, anthraquinone, and sulfur are also effective. However, these materials provide undesirable color in the resulting coating, or are impermanent under some conditions, or tend to discolor or otherwise adversely affect surfaces of other papers or articles with which they may come in contact during storage, or are insufficiently sensitive to visible light, or are less desirable for other reasons.

A much preferred type of photoelectrosensitive copying-paper, having more desirable initial appearance as well as better storage qualities, is prepared from photoelectrosensitive materials of the class represented by zinc oxide, zinc sulfide, yellow cadmium sulfide, titanium dioxide, barium titanate, and various phosphors such as those based on zinc oxide, zinc sulfide and cadmium sulfide, or mixtures thereof.

The backings or supporting sheet materials of this invention are electrically conductive in comparison with the relatively high-resistivity sensitive surface. Under normal humidity conditions, untreated paper is found to be usefully conductive. Regenerated cellulose transparent film (cellophane) is particularly effective. Somewhat increased conductivity might be obtained by incorporating conductive salts in the paper backings, for example by treating the paper with aqueous solutions of sodium sulfate or the like; but the conductivity of the resulting product varies with the humidity of the surroundings, and background areas of prints produced on such papers are frequently badly fogged. Non-hygroscopic particulate conductors such as acetylene black or aluminum flake have been incorporated in paper backings to provide increased electrical conductivity; but the conductivity of such sheets is not uniform and the product may be off-color. Metal plates or foils are effective but are expensive, difficult to handle, and have other disadvantages.

It has been found that much superior results are obtained by providing a continuous conductive but very thin metallic layer directly beneath a coated light-sensitive layer. Further description of the products and processes of this invention will accordingly be provided primarily in terms of such preferred structure, which is specifically illustrated in FIGURE 2, in which the conductive backing **20** is indicated as including a flexible

base 22, e.g., of paper, and a thin conductive surface coating 23 which may be of vapor-deposited aluminum or very thin adherently attached aluminum foil. The foil-coated paper is particularly desirable since a surface of improved smoothness is thus provided, resulting in more accurate and sharply defined reproductions.

The metallized conductive backings as just described may be directly electrically connected to the power supply, in which case the support 13 need not be conductive and may be eliminated, e.g., in the case of continuous strips from rolls of the sheet material, supported under tension between connecting clamps.

The adverse effect of variations in humidity on the conductivity of certain types of backing members is avoided in the preferred sheet materials of this invention as above noted. Conditions of high humidity may have other adverse effects; for example, coatings of zinc oxide in polystyrene binder have developed excessive background color when used for electrophotographic copying under humid conditions. It has been found that the adverse effects of high humidity are minimized or eliminated by the addition to the coating of small amounts of water-resistant metallic soaps, such as of the order of one or two percent by weight of zinc stearate or cobalt palmitate. The amount required varies directly with the humidity to which the sheet is to be subjected. These additives are found to contribute also to permanent smoothness and lack of graininess in the photoelectrosensitive surface, and to increase the firmness of bond between the coating and the underlying metallic surface. The polyvalent metal higher fatty acid soaps have also been used to alter the properties of the sheet with respect to light-sensitivity; for example, addition of small amounts of cobalt soaps has been found to render a light-sensitive zinc oxide coating sensitive to a much wider range of color values. Again, these metallic soap additives stabilize the photoelectrosensitive coating against the graininess of image sometimes encountered with copy-sheets after prolonged aging in the absence of such additive materials.

Since the preparation of visible reproductions of printed matter such as letters, pictures, diagrams, pages of books or magazines, etc., is one of the principal fields of utility for the present invention, the material used to produce the aerosol required for developing the reproduction is customarily a black or distinctly colored substance. Certain classes of dyestuffs have been found to be particularly well adapted for this purpose. They are permanently stable under normal room and storage conditions; they do not vaporize at normal temperatures to cause discoloration of adjacent surfaces, nor do they fade or discolor unduly on exposure to sunlight. They vaporize without decomposition when heated rapidly to operable elevated temperatures, and the resultant aerosol is readily deposited on the sensitive surface under the influence of the high potential. Typical dye products which have been found satisfactory for the purposes of this invention include the following: Alizarine Irisol N; Brilliant Oil Blue; Anthraquinone Sky Blue B Base; Oil Red O; Oil Yellow; Oil Brown O; and Oil Brown N.

Certain dyestuffs form aerosols which, when applied to some copy-sheets as herein noted, are impermanently attached and may be removed, or at least re-distributed, by rubbing or brushing. Other dyestuffs, on the contrary, and in particular those which melt or fuse or otherwise become liquid, plastic, or at least somewhat sticky during volatilization, are found to adhere strongly to the copy-sheet and to form substantially completely smudge-proof prints. The same result has been accomplished with the former class of dyestuffs by adding thereto small amounts of fusible material such as waxes or plasticizers. These apparently combine with the dyestuff to produce a mixture which on volatilization is at least temporarily tacky and therefore becomes strongly adhered to the copy-sheet immediately on contact. Hence for best results in terms of permanent visible smudge-proof prints it is desirable to employ as the developer material a dyestuff or mixture which, on volatilization, forms an at least temporarily tacky condensate which does not immediately recrystallize or harden to a non-tacky state.

The practice of the invention is not limited to the use of vaporizable dyestuffs or colored materials, since visible images may be produced by deposition of various chemically or physically active aerosols on properly prepared receptor surfaces. Copying-paper prepared for such operations may be more expensive and troublesome to produce, and the time required for development may be somewhat greater; but the process nevertheless has a number of advantages when compared to development with dyestuffs. The developer material may be colorless, so that it does not stain or discolor surfaces with which the free aerosol may accidentally come in contact. Delayed printing and other novel effects are made possible.

As an example of a physical developing action, a suitable soluble dyestuff is dispersed in the form of particles in the light-sensitive coating and activated with an aerosol developer formed of a solvent material which dissolves and spreads the dyestuff to provide a visible mark. A specific example of such a product and process employs Alizarine Irisol N as the dyestuff, uniformly and minutely dispersed in a coating of zinc oxide particles in a polyvinyl acetate binder applied in aqueous dispersion form and then dried. The dispersed particles of the dyestuff give only a faint tint to the coated surface. An intense visible image is developed when the sheet is subjected to patterned deposition of resorcinol in aerosol form and then warmed, the resorcinol dissolving the dye particles and spreading the dissolved dye to provide the visible image.

Resorcinol is a stable volatilizable solid which in liquified form is a good solvent for the dyestuff employed. Many other solvents, both liquid and solid, e.g., amyl or butyl monoesters of ethylene glycol, cyclohexanol, acetophenone, stearic acid, and 8-hydroxyquinoline have also been found effective. Of these, the solids are most effectively applied by volatilization as hereinbefore described, whereas useful aerosols of the liquid materials may be produced either by rapid heating or in other ways.

In a modification of the above-described system, the copying-paper is provided with a strongly colored surface which is then masked with a soluble protective surface coating, such as a thin microporous film of blushed lacquer. The photoelectrosensitive component may be located just below or partly within the lacquer film, but is preferably placed within the colored layer, since in that position it is closer to the conductive backing while still being accessible to illumination through the blushed lacquer masking layer. Activation of the sheet with a light-image, and application of an aerosol of a solvent material capable of dissolving and rendering permanently visibly transparent and continuous the normally visibly opaque discontinuous blushed lacquer coating, while maintaining a high potential on either the sheet or the electrode or both, all as hereinbefore described, provides for the local transparentization of the coating and exposure to view of the underlying color layer in the pattern of the light-image. With cellulose lacquers, solvent developer materials such as the volatile ethylene glycol monoalkyl esters or various known non-volatile liquid or solid plasticizers are found to be effective when applied in aerosol form.

In many instances the binder by which the photoelectrosensitive material is supported on the sheet material is also susceptible to the solvent action of the solvent aerosol. Dissolved dyestuff is then caused to blend uniformly with the binder at the solvated area and imparts

a highly effective coloration to the sheet in the areas defined by the light-image.

One important advantage of such solvent-action processes is the substitution, for the dye aerosol with its tendency to discolor adjacent areas, of the colorless solvent aerosol, any excess of which subsequently volatilizes and is harmlessly dissipated. Another advantage is the formation of permanent images with no possibility of subsequent smudging.

Colored prints or copies may similarly be produced with colorless or non-staining aerosols by a process of chemical development. As an example of a chemical developing action, the light-sensitive coating is provided with a content of ferric stearate as one reactant, and pyrogallol or catechol in aerosol form is selectively deposited thereon by methods already described, the resulting chemical reaction between the iron compound and the phenol providing a permanent visible mark exhibiting a high degree of contrast. Here again, warming of the treated sheet is frequently desirable in obtaining complete reaction of the color-producing components and in providing a permanent image.

Other iron soaps such as ferric laurate, myristate and caprylate may replace the ferric stearate in the copying-paper and the image may be developed with aerosols of iron-reactive phenols such as 8-hydroxyquinoline, propyl gallate, protocatechuic acid, catechol, gallic acid, pyrogallic acid, or resorcinol. Other pairs of reactants and developers include nickel stearate and dimethylglyoxime; manganese, magnesium, copper, silver or cobalt soaps and phenolic materials; various heavy metal soaps with thiourea, benzotriazol, or 2-mercaptobenzimidazol; stabilized diazonium salts and phenolic materials; and various other reactants, aerosol developers, and combinations thereof. For example, room-temperature chemical developing action is attainable by employing an aerosol of "chloranil" (tetrachlorobenzoquinone) with a photoelectrosensitive receptor sheet having a surface coating of Du Pont "Hectograph White A," a stabilized colorless triphenylmethane dye.

As an alternative to the step of heating the treated sheet material which has been exposed to an aerosol of a normally solid developer material, a high-boiling liquid solvent component may be vaporized and selectively deposited together with the solvent or reactant material of either the physical or the chemical systems just described. The system is particularly effective with copy-sheets containing particles of interreactive color-forming reactant materials. The liquid solvent penetrates the binder component of the light-sensitive coating and permits effective contact of the chemically interreactive image-producing materials, but subsequently becomes dissipated within the much greater bulk of the binder which then seals and protects the image.

The application of solvent-type materials in aerosol form is useful also in permanentizing images produced by direct deposition of dyestuffs. Volatile or normally non-volatile solvent or plasticizer materials which soften the binder component of the copy-sheet and render it slightly sticky, or which similarly soften and tackify the developer material itself, cause the aerosol dye particles to adhere firmly to the copy-sheet and thus provide a permanent and non-smudging image.

Other colorless or non-staining aerosols have been used to provide lithographic patterns from which large numbers of copies are printed by conventional lithographic duplication methods. For example, an organophilic waxy developer material such as paraffin in aerosol form is applied to pattern areas on a copying-paper having a hydrophilic surface, such as may be obtained by rubbing the sensitized sheet with a minimum amount of finely powdered aluminum silicate. The sheet is used in applying organic inks to paper by lithographic transfer, the oily ink being selectively picked up on the paraffin-coated areas and transferred to a lithographic blanket while being prevented from adhering to the adjacent water-moistened hydrophilic areas. Somewhat analogously, images produced with aerosols of soluble dyes on solvent-resistant copying-papers are transferred to paper by spirit duplication or hectographic methods. Multi-colored images are readily prepared by this latter method.

The following examples will further serve to illustrate the principles of the invention but are not to be considered as limitative.

Example 1

Dense high-quality smooth-surface paper was coated on one surface with an extremely thin layer of aluminum applied by vapor deposition under vacuum. The aluminum surface was brilliantly reflective. Over this coating was then applied a thin continuous uniform coating of a viscous mixture prepared by uniformly dispersing 55 parts by weight of zinc oxide powder in a solution of 5 parts of a styrene polymer in 40 parts of toluene, and the coating was dried at moderately elevated temperature. The dried layer was about one mil (.001 inch) in thickness. The styrene polymer employed was a copolymer of a predominant proportion of styrene with a small proportion of butadiene, obtainable as "Pliolite S–5"; it is capable of forming self-sustaining tough flexible thin films, and is substantially non-conductive of electricity. The zinc oxide, Merck's "Analytical Reagent" grade, had a particle size in the approximate range of 0.1–0.5 microns or somewhat larger.

The coated sheet, about 7 x 7 inches in size, was placed in an apparatus as indicated in FIGURE 1, being supported against a grounded flat metal plate with the coated surface disposed outwardly. The image source **10** was located at a distance of 36 inches from the support and consisted of a 35 mm. Leica Prado-150 projector, operated with a 100 watt bulb and at a lens opening of about *f*–8. The corona source **11** was a single point source located at a distance of 10 inches from the surface of the support. A negative potential of 50,000 volts was impressed on the point, the other side of the voltage source being grounded. The assembly was maintained in dim light, and an image of a negative line drawing was focused on the coated sheet. An aerosol was produced at source **14** by heating the wire **141** to substantially instantaneously vaporize the developer coating **142**. The developer material in this case was Du Pont Oil Brown O, a dark brown anthraquinone dye. A short exposure, sufficient only to permit the aerosol to rise past the face of the support, produced an enlarged reversed reproduction of the original negative on the sensitive sheet, in the form of a brown line drawing on a white background.

The reproduction was characterized by extremely fine detail and sharp contrast. The white background was substantially free of dye, whereas the lines of the reproduced drawing were sharply defined and uniformly dense. However the shadow of the corona source **11** produced visible discontinuity in the reproduction.

The specific developer material mentioned above produced a substantially smudge-proof and permanent print. Substitution of Alizarine Irisol N for the Oil Brown O resulted in a print showing an undesirable degree of smudging when rubbed with the fingers or against a clean sheet of paper. Smudging was eliminated by blending with the Alizarine Irisol N a small amount of paraffin, as previously described herein. Smudging was equally effectively eliminated by adding a small amount of paraffin or paraffin oil to the binder solution used to prepare the copy-sheet. The presence of this tackifier material at the surface of the copy-sheet served to retain the extremely fine particles of the aerosol developer, and to prevent smudging, without producing any degree of stickiness which was observable to the touch or detrimental to the normal use of the copy-sheet.

The copying-paper was held against the metal support plate by means of spring clips having toothed edges which penetrated the surface layer and provided for electrical

contact between the metallic layer of the copying paper and the grounded support plate. In the absence of such clips, effective contact is frequently formed through tiny arcs set up between the metal plate and the metallic layer along the edges of the sheet. Adequate contact may also also be established through the thickness of the paper backing.

Example 2

In this example a grid of wires replaced the point corona source of Example 1. The grid was formed of fine wires parallel to each other and at a distance of 2 inches from each other, the whole being placed at a distance of 3 inches from the front of the sensitive paper, and oscillated as shown in connection with FIGURE 4. The metal support plate was charged at 20,000 volts positive and the grid at 20,000 volts negative from a suitable source of rectified A.C. Alizarine Irisol N was used as the aerosol developer material.

A photographic negative was employed as an image source, the image being projected and focused on the sensitive paper just prior to and during the evolution of the aerosol. A blue positive copy was obtained having good contrast and detail.

In a variation of the above, the metal plate is charged at 40,000 volts positive while the grid is connected directly to ground. The quality of the print produced remains unchanged. The electrical system is simplified. The same variation is equally applicable to the system described under Example 1.

Somewhat less intense reproductions are obtained by reducing the voltage at each of the plate and grid to 10,000 volts.

Example 3

This example duplicates Example 2, except that the source of potential is disconnected from the grid just before the aerosol is generated. The source of potential remains connected to the plate, and the light-image remains focused on the sheet. There results a copy having reduced background color and more uniform distribution of the aerosol particles from the bottom to the top of the sensitive sheet, although being of somewhat diminished intensity.

Example 4

Many photoelectrically sensitive materials have an effective "light memory" so that development may be accomplished at some period after the light-image has been withdrawn but while the copy-sheet is still under the influence of such light-image.

The sensitive paper of Example 1 is irradiated through a photographic negative by means of a contact printer, as used for photographic processing. The sheet is then placed on the vertical metal support plate, voltage is impressed on the metal plate and on the grid, and an aerosol is generated and allowed to rise past the sensitive sheet, as in Example 2. These latter operations are conducted in semi-darkness, and several of the previously exposed sections may be developed simultaneously or in immediate succession as desired. A fully satisfactory positive print is obtained where development is carried out within about 10 minutes after exposure. At longer intervals the resulting copy becomes progressively weaker.

Approximately the same degree of exposure to light is used in the above processes as is found effective in typical photographic procedures. The exposure may be obtained with a conventional contact printer or with a flashbulb or with exposures of even shorter duration, such as are obtained with stroboscopic sources of illumination used in photography. Dynamic development with the aerosol, under the influence of the continuously maintained high potential, may require substantially greater time than is required for the exposure; but several exposed segments or frames may undergo development simultaneously, so that exposure and development may proceed continuously and at the same rate.

Example 5

This example describes the production of multiple color prints by the processes of this invention.

The sensitive sheet was in this case formed by coating the previously metallized paper backing of Example 1 with a mixture of zinc oxide and styrene resin containing 0.01 percent, based on the weight of zinc oxide and resin, of "Pontachrome" Azure Blue B Conc. 200%. The dry thickness of the coating was about 1½ mils and the sheet was essentially white in appearance.

In the apparatus of Example 2, an image obtained from a blue and red transparency through a blue-green cyan filter was developed with a blue aerosol of the dyestuff employed in Example 2, and the image obtained from the same transparency through a yellow filter and superimposed on the first image was developed with a red aerosol of Celanthrene Red YP. The two colors blended to produce an effective two-color positive print with very little background color.

Yellow cadmium sulfide may be used in place of the combination of zinc oxide and blue dye in the sensitive sheet material to produce equally effective multi-color sensitivity. The yellow appearance may be effectively masked without appreciable reduction in photoelectrosensitivity by over-coating with a thin layer of titanium dioxide pigment, e.g., in a polyvinylbutyral binder.

A three-color print was similarly produced on a sheet of metallized paper coated with a mixture of 80 parts of zinc oxide, 20 parts of zinc oxide which had previously been treated with "Azure Blue B" dye, and 100 parts of a 1:12 solution of "Parlon" chlorinated rubber in toluene. An alcohol solution of the dye was added to the zinc oxide which adsorbed a portion of the dye, the remainder being removed by washing with alcohol. Other ratios of treated and untreated zinc oxide are useful, higher proportions of the treated oxide giving increased green and red sensitivity but also causing a blue tint in the sensitive coating. The dry coating thickness was about 1½ mils. A colored photographic negative of a three-color subject, such as is obtained on "Kodacolor" film, was used as the original. The image formed through a Wratten No. 47–B blue filter was developed with an aerosol of Oil Yellow dye. The superimposed image formed through a Wratten No. 61 (N) green filter was next developed with an aerosol of "Celanthrene Red YP" red dye. Similarly, the image formed through a Wratten No. 29 (F) red filter was then developed with an aerosol of "Brilliant Oil Blue" dye. The resulting print showed color values analogous to those of the three-color subject.

The panchromatic properties of a sheet employing a mixture of treated and untreated zinc oxide particles in the sensitive layer are at a maximum when the treated particles carry a dye which is absorptive of red and green light. Sheets made with zinc oxide pigment but having increased sensitivity to red light are produced by employing zinc oxide sensitive pigment which has been treated with a blue dye. Analogous modifications of other sensitive particulate materials may be made.

Example 6

In this example the apparatus and procedure is the same as described under Example 2, except that, just prior to the generation of the aerosol, and with the light-image remaining impressed on the sheet, the voltage is reversed on both the metal support plate and the grid. Generation of the aerosol then results in a negative rather than a positive print of the negative transparency, i.e., the aerosol is deposited on the unlighted rather than the light-struck areas. The same procedure may be used to provide positive prints of positive transparencies.

Such prints may equally well be made by reversing the polarity on the plate while disconnecting or grounding the grid.

The zinc oxide of the copying-paper described in Example 1 provides a white surface which is highly effective

as a background for the colored dyes employed in developing the copies. Other sensitizing materials may be of equal or greater effectiveness as a light-sensitive component under exposure to a light-image, but may be much less effective as a background component. Cadmium sulfide, for example, is yellow-orange in color and is ineffective as a background material with dyes of similar color even though it provides a high degree of sensitivity. It has been found, however, that a thin surface coating may be applied over a sensitive cadmium sulfide layer to give an improved print background without destroying the sensitivity of the copying-paper. Thus, a minimum surface layer of titanium dioxide pigment in film-forming binder applied over a sensitizing layer of cadmium sulfide in the same binder on a suitable backing member results in an effective copying-paper with good sensitivity as well as excellent background characteristics. The titanium dioxide is itself somewhat light-sensitive but is here employed primarily as a background material.

Mixtures of photoelectrosensitive materials provide additional advantages over the individual materials in many instances. One particular example employs a mixture of one part of Merck's Reagent Grade zinc oxide and three parts of New Jersey Zinc "Cryptone #800" zinc sulfide as a replacement for the zinc oxide of the sheet material of Example 1. The sheet provides greatly increased tonal range in continuous-tone reproductions produced, for example, in accordance with the procedures of Example 2. Such a sheet may be effectively sensitized with a dye, e.g., as indicated in connection with Example 5, where panchromatic properties are desired.

Some conductivity in the backing member is necessary in order to establish the necessary difference in surface potential between the locally illuminated and darkened areas of the copying-paper. The extent of current flow required is extremely minute, as may be understood from the fact, previously referred to, that untreated paper under normal humidity conditions may serve as a useful base web for the copy-sheets of this invention. Such a paper-backed copy-sheet may be clamped against a conductive metal plate **13** as in FIGURE 1 of the drawing, but must in such event be in close contact with the entire plate since printing is less effective in areas of pour contact. This latter difficulty is effectively overcome by supporting the paper copysheet only along the edge areas, e.g., on a frame rather than a continuous plate; which again illustrates the low degree of conductivity required in the copy-sheet backing. Uniform printing across an entire 8½ x 11 inch copy-sheet is obtainable using a conductive frame covering only a one-half inch margin. The very low current drain required for aerosol deposition permits the sheet to be held at the charging potential over its entire area.

As the volatilized developer material produced at the element **14** of FIGURE 1 passes across the face of the sensitized copying-paper, particles are deposited on the sensitized surface in accordance with variations in the light-image to which the sheet is or has been exposed. The corona discharge, e.g., from the point source **11** of FIGURE 1 or the line sources **43** of FIGURE 4, intensifies the deposition, presumably both by charging the aerosol particles and by maintaining maximum potential difference at the plate surface. The added charge is desirable but not essential, as noted in connection with Example 3. A charge may additionally be impressed on the aerosol particles as they are first formed, for example from a probe electrode source of corona placed directly above the aerosol source **14** of FIGURE 1 and below the face of the sheet **12**, the properly charged particles then being more forcefully attracted to appropriate areas of the exposed sheet. Such a system may be combined with the previously described source of corona **11** or **43** to provide a variety of results. For example, reversing the polarity of the aerosol particles by reversing the polarity of the probe electrode permits the preparation of negative or positive prints as desired.

The light-sensitive coating which is applied over the conductive backing in the preferred copy-sheets of this invention comprises a sensitive pigment or powder which ordinarily will be dispersed in a film-forming binder of comparatively high resistivity. The relative proportions of these two components should be in the neighborhood of 5:1 to 20:1, these proportions being expressed in terms of weights of zinc oxide and polymer as specified in Example 1. With other materials having different unit weights, the ratios are properly compared on a volume basis. Less than approximately the minimum indicated amount of binder may result in blurred backgrounds in the reproductions, although useful copies of line drawings have been made on copying-papers produced by applying zinc oxide powder to a binder-coated aluminized paper sheet, with substantially no binder film being present between adjacent particles. Excessive amounts of binder on the other hand limit the contrast and intensity of the reproduction. Blurring is also obtained with coatings in which the binder component is unduly conductive, for example in copy-sheets containing significant amounts of acidic dyestuffs or conductive salts.

The thickness of the sensitive coating is also rather critical if best results are to be had. With the formula of Example 1, finished coatings of about ½ to 10 mil thickness have given best results. The thicker coatings are ordinarily reserved for compositions in which particles of larger diameter are used. For example, a one-mil coating is specified in Example 1 for Merck's "Analytical Reagent" grade zinc oxide, a French process oxide having an average particle size in the range of about 0.1–0.5 micron, whereas oxides having a particle size up to 5 microns would ordinarily require a dry coating thickness greater than one mil. Particles up to 25 microns in diameter have been found useful, and are best employed in still thicker coatings. However the energy absorption appears to be more effective with particles in the range of 0.1–5 microns, or preferably 0.1–1.0 micron, average diameter.

In some instances the sensitive material has been employed in the absence of an insulating film-forming binder. Thus, zinc and cadmium plates, or metal sheets having a surface plating of zinc or cadmium, have been converted at the surface to zinc sulfide and cadmium sulfide respectively by appropriate treatment, and the extremely thin sulfide layers have been found to be light-sensitive and to permit the reproduction of light-images by the methods herein described. The direct application of the sensitive material in powder form to the paper pulp from which the sheet material is produced has been described previously herein.

The invention provides a direct method for the duplication of sketches and drawings, typewritten correspondence, printed books and papers, photographs, and various other examples of graphic matter. It is particularly applicable to printing of positives directly from photographic negatives. It provides a means of enlarging and copying microfilm at rapid rates and in an effective and economical manner. The invention also provides a method for direct and instantaneous photography, being applicable to the direct formation of photographs in full color as well as in monochrome and without any intermediate processing. Multiple photography is likewise made possible by the methods described. For example, a series of exposures on a continuous sensitized strip, e.g., a strip composed of a minimum coating of a mixture of zinc oxide and zinc sulfide bonded to a transparent backing such as cellophane, provides the equivalent of a cinematographic or "movie" film when developed in accordance with the principles established in Example 4. Exposure and development require only a few seconds, and the completed film is then immediately ready for viewing. The same is true of photographs or copies

made by X-ray or other effective invisible radiation, which, for the purposes of this invention, may be considered as being capable of forming a "light-image"; the total process is extremely rapid, copies being available within seconds after the exposure and without chemical processing. Modifications of the process, particularly with respect to the type of aerosol material, make possible the equally rapid preparation of printing-plates for lithographic and hectographic duplicating processes; and these also may be considered as examples of graphic representations even though the developed images may not be directly visible. Numerous other modifications falling within the ambit of the invention will be apparent in view of the disclosures and teachings here provided.

What is claimed is as follows:

1. The method of electrophotographic printing which comprises optically projecting through the atmosphere directly onto the front of a photoconductive insulating layer carried on an electrically conducting paper support, a sharp negative optical image of radiation to which the layer is sensitive, simultaneously creating an electrical corona discharge in the atmosphere in front of the layer at an electrical potential difference from said support, directing a suspension of developer particles into the path of said image projecting radiation and into the corona discharge which is of sufficient intensity to cause deposition of the particles onto the photoconductive layer in a pattern corresponding to the optical image.

2. The method for electrographic printing which comprises projecting an image of radiation through the atmosphere directly on to the front of a photoconductive insulating layer which is sensitive to said radiation carried on an electrically conducting support to form a differentially conductive pattern in said photoconductive layer corresponding to said image, while said differentially conductive pattern is still present in said photoconductive layer creating an electrical corona discharge in the atmosphere in front of the photoconductive layer at an electrical potential difference from said support, and directing a suspension of developer particles into the path of the corona discharge which is of sufficient intensity to cause dynamic deposition of the particles on to the photoconductive layer in a pattern corresponding to the image.

3. The method for electrographic printing which comprises creating a differentially conductive pattern by exposing to a pattern of radiation a photoconductive layer which is sensitive to said radiation carried on an electrically conducting support to form a differentially conductive pattern in said photoconductive layer corresponding to said image, while said differentially conductive pattern is still present in said photoconductive layer creating an electrical corona discharge in the atmosphere in front of the photoconductive layer at an electrical potential difference from said support, and directing a suspension of developer particles into the path of the corona discharge which is of sufficient intensity to cause dynamic deposition of the particles on to the photoconductive layer in a pattern corresponding to the image.

4. The method for electrophotographic printing which comprises projecting an image of radiation through the atmosphere directly on to the front of a photoconductive insulating layer which is sensitive to said radiation carried on an electrically conducting support to form a differentially conductive pattern in said photoconductive layer corresponding to said image, subsequently within a finite time and while said differentially conductive pattern is still present in said photoconductive layer creating an electrical corona discharge in the atmosphere in front of the photoconductive layer at an electrical potential difference from said support, volatilizing a volatilizable printing material to form an aerosol of extremely small uniform particles, and directing said aerosol into the path of the corona discharge which is of sufficient intensity to cause dynamic deposition of the aerosol particles on to the photoconductive layer in a pattern corresponding to the image.

5. The method for electrophotographic printing which comprises projecting an image of radiation through the atmosphere directly on to the front of a photoconductive insulating layer which is sensitive to said radiation and which contains a first reactant carried on an electrically conducting support to form a differentially conductive pattern in said photoconductive layer corresponding to said image, while said differentially conductive pattern is still present in said photoconductive layer creating an electrical corona discharge in the atmosphere in front of the photoconductive layer at an electrical potential difference from said support, volatilizing a volatilizable printing material comprising a second reactant to form an aerosol of extremely small uniform particles, and directing said aerosol into the path of the corona discharge which is of sufficient intensity to cause dynamic deposition of the aerosol particles on to the photoconductive layer in a pattern corresponding to the image for visible reaction with said first reactant.

6. The method for electrophotographic printing which comprises projecting an image of radiation through the atmosphere directly on to the front of a photoconductive insulating layer which is sensitive to said radiation and which comprises a readily soluble component carried on an electrically conducting support to form a differentially conductive pattern in said photoconductive layer corresponding to said image, while said differentially conductive pattern is still present in said photoconductive layer creating an electrical corona discharge in the atmosphere in front of the photoconductive layer at an electrical potential difference from said support, volatilizing a volatilizable printing material comprising a solvent for said soluble component to form an aerosol of extremely small uniform particles, and directing said aerosol into the path of the corona discharge which is of sufficient intensity to cause dynamic deposition of the aerosol particles on to the photoconductive layer in a pattern corresponding to the image.

7. The method for the electrophotographic production of a differentially wettable print which comprises projecting an image of radiation through the atmosphere directly on to the front of a photoconductive insulating layer which is sensitive to said radiation carried on an electrically conducting support to form a differentially conductive pattern in said photoconductive layer corresponding to said image, while said differentially conductive pattern is still present in said photoconductive layer creating an electrical corona discharge in the atmosphere in front of the photoconductive layer at an electrical potential difference from said support, volatilizing a volatilizable printing material to form an aerosol of extremely small uniform particles, and directing said aerosol into the path of the corona discharge which is of sufficient intensity to cause dynamic deposition of the aerosol particles on to the photoconductive layer in a pattern corresponding to the image, one of said photoconductive surfaces and said printing material being hydrophilic and the other being organophilic.

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