July 11, 1967 W. SIMM ETAL 3,330,683

METHOD OF DEVELOPING AN ELECTROSTATIC IMAGE WITH AN ELECTRICALLY CHARGED LIQUID AEROSOL

Original Filed April 13, 1962

4 Sheets-Sheet 1

FIG. 1

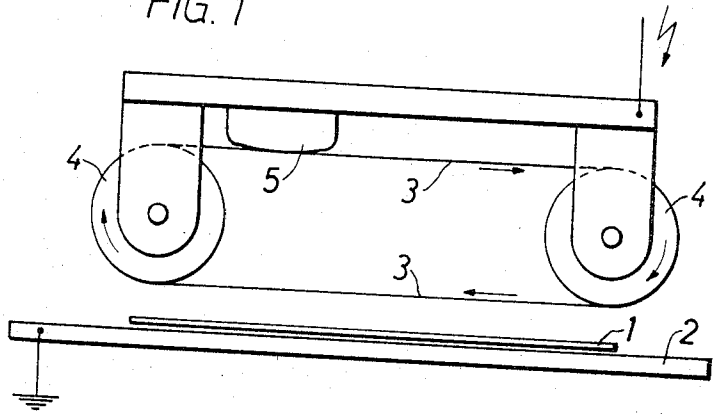
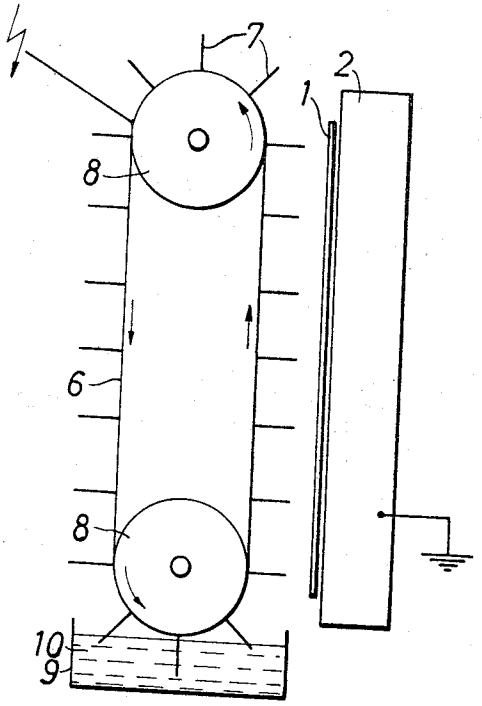


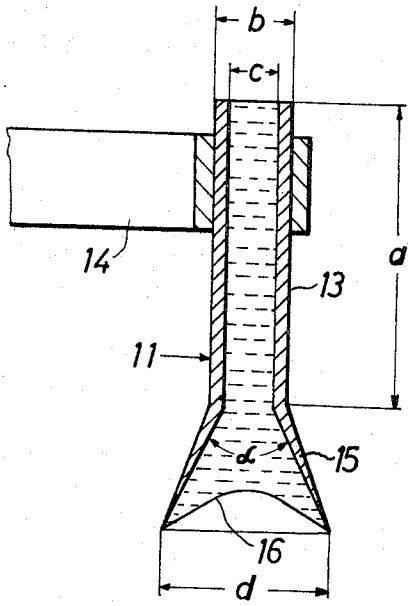
FIG. 2



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FIG. 3

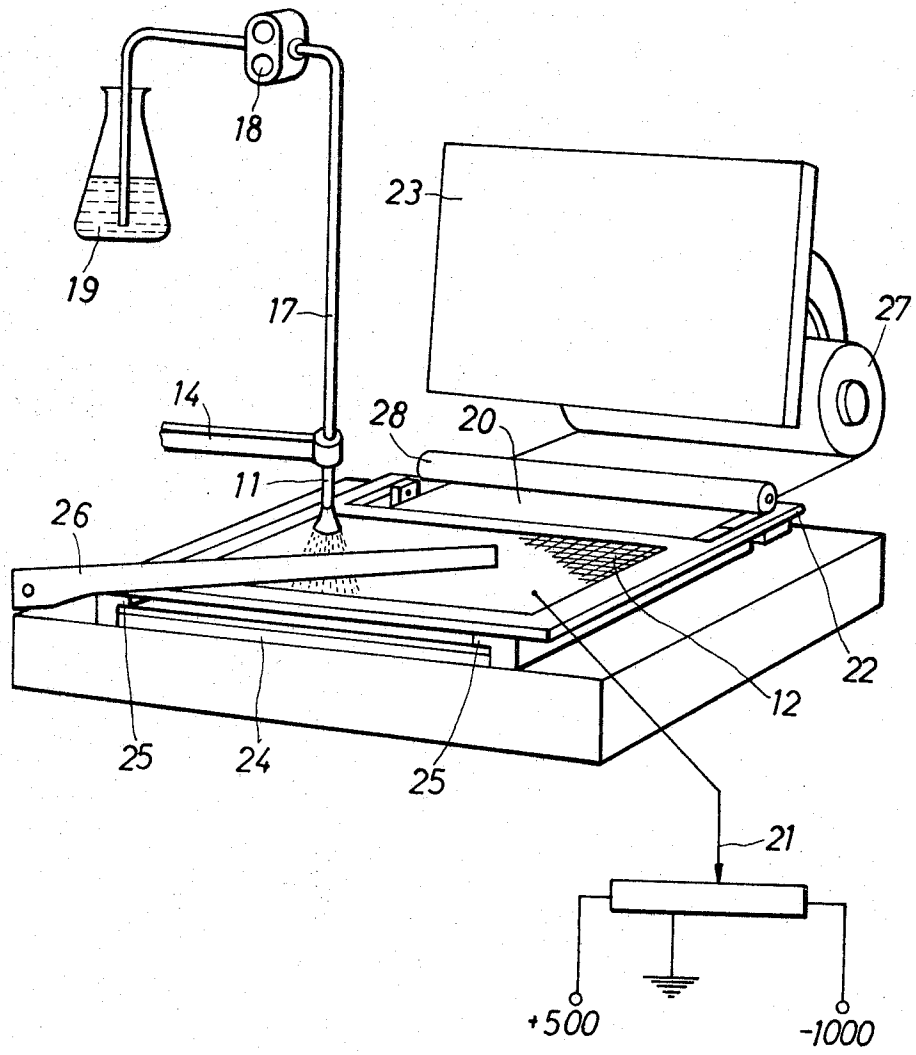




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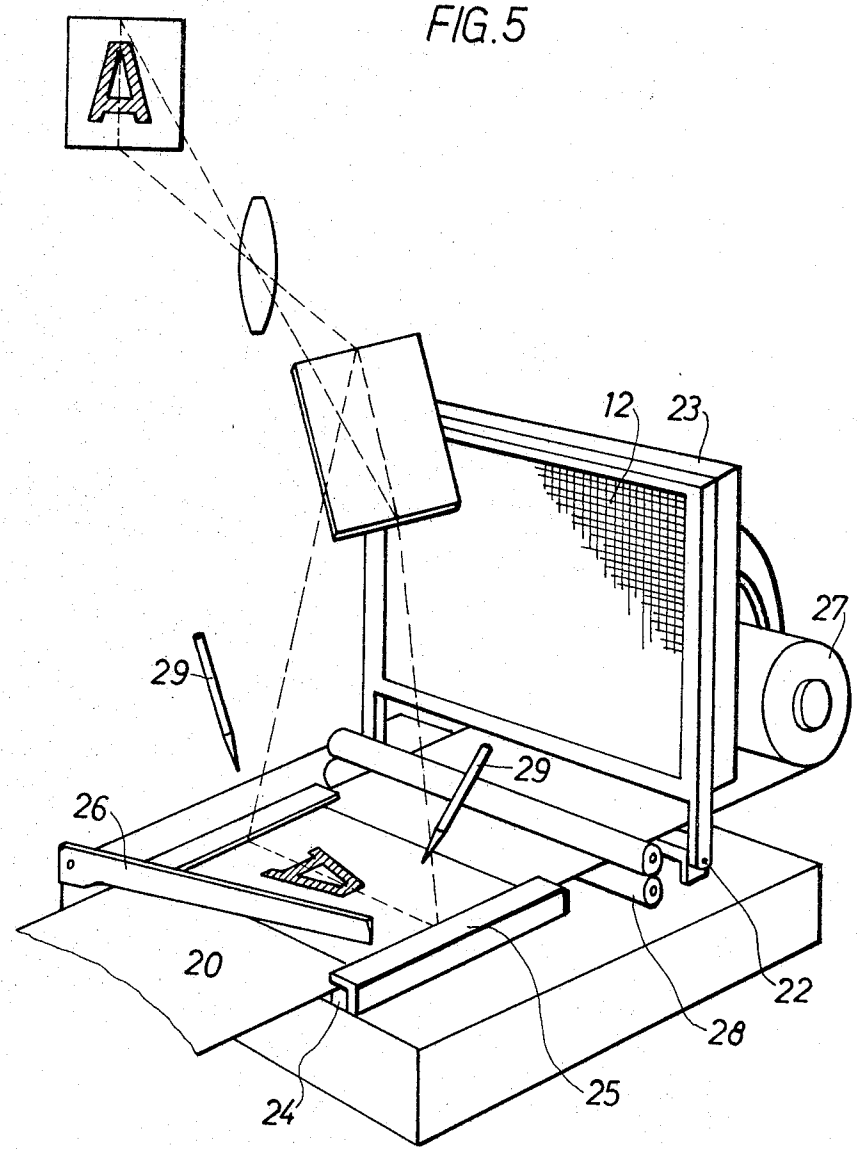
FIG. 4



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FIG. 5



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3,330,683

METHOD OF DEVELOPING AN ELECTROSTATIC IMAGE WITH AN ELECTRICALLY CHARGED LIQUID AEROSOL

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Continuation of application Ser. No. 187,426, Apr. 13, 1962. This application Sept. 22, 1965, Ser. No. 497,584

Claims priority, application Germany, Apr. 26, 1961, F 33,767; Mar. 8, 1962, F 36,217

2 Claims. (Cl. 117—37)

This application is a continuation of application Ser. No. 187,426, filed Apr. 13, 1962, now abandoned.

This invention relates to the development of electrophotographic latent images and, more particularly, to an improved method and apparatus for developing such images with the aid of an aerosol.

According to conventional electrophotographic processes, a photoconductive layer is electrically charged and exposed to a light image to be recorded. Charge dissipation in the light-struck areas results in a latent electrostatic image corresponding to the dark areas of the original. This latent image is thereafter developed with the aid of an electrically charged toner or colored aerosol. For the production of the charged image, a negative charging is generally employed, the charging of the toner or aerosol then being chosen to be negative or positive, according to whether the developed image is to be negative or positive with respect to the original.

According to a significantly different process, a conductivity pattern is formed by image-wise exposure on a photoconductive layer which is not charged beforehand (for example a zinc oxide layer) which image remains held for a relatively long period of time, also after exposure, and this conductivity pattern is made visible with the aid of colored aerosols and using a stream of ions emitted by a corona discharge device.

In both cases, aerosols of liquid dyestuff solutions can be used advantageously for the development because, by a suitable choice of the solvent, the image produced is automatically fixed since the dyestuff solution is sucked up by the photoconductive layer. On the contrary, if dry toner powder is used, then in addition the powdered material has to be melted or to be dissolved with suitable solvents for the fixing.

For the production of liquid aerosols with a sufficiently fine drop distribution (size of the droplets, about 1μ or similar) it is known to use nozzles which are operated with compressed air (or other gases). Compressors are for example used for the production of the compressed air and this constitutes an undesired expense as regards equipment. Since the liquid aerosols cannot be readily charged by friction or contact, which is possible with toners in powder form, the charging operation necessitates a separate device, for example, the arrangement of electrodes which generate a corona, whereby some of the aerosol is lost by electrical deposition. On the other hand, not all the aerosol particles can be utilized in practice for the image development, since the gas stream entraining the aerosol particles always carries a residue of the aerosol from the actual development device. As a result, not only is a certain part of the aerosol lost, but in addition separate cleaning devices are necessary for the escaping air.

It is among the objects of the instant invention to avoid the disadvantages described above and to provide a simple and inexpensive technique for developing electrophotographic images with an aerosol.

FIG. 1 is a schematic view of one embodiment of this invention;

FIG. 2 is a schematic view of another embodiment of this invention; and

FIGS. 3–5 are schematic views of still another embodiment of this invention.

It has now been found that the production and charging of the aerosol is substantially simplified and can be carried out with considerably less equipment if the liquid is atomized electrostatically by means of electrodes having a strongly curved surface. Use is made in this case of the fact that certain liquids are atomized into individual particles at the tips of edges of high-voltage electrodes solely by the strong, non-homogeneous, electric fields occurring at the said places, the size of said particles depending inter alia on the nature of the liquid, the value of the electrode voltage and the form of the electrodes. The atomization by means of non-homogeneous electric fields is known per se and is used in practice in electrostatic lacquer-spraying plants, very high voltages of for example 100 kv. being required in such cases. The metal electrodes necessary in this case are not suitable for electrophotographic development, since they produce droplets which are too large, spray off too much liquid and require too high a voltage. By special construction of the spray-type electrodes, it has now become possible for dyestuff solutions which can be used for electrophotographic image development to be atomized so finely in a small space and with relatively low voltages of 5–40 kv. that they can be utilized by spraying on to the photoconductive layer directly for the development of electrostatic images or conductivity pattern.

Structures having a strongly curved surface (for example electrodes in the form of filaments or bristles with a thickness of 0.01 to 0.5 mm.) are suitable for the production of an extremely fine mist of liquid in the quantities required for the development of the image. The surface of said electrodes is constantly wetted with the liquid which is to be sprayed. An extremely fine atomization is produced if the electrodes for example the filament or bristle itself consists of a material which is not electrically conducting, for example a synthetic plastic, and if only the surface is made sufficiently conductive for the spraying effect by wetting with the liquid which is to be sprayed. As materials for the filament or bristles, numerous synthetic or natural polymers are suitable for example: polyamines (nylons) such as condensation products of w-amino-undecanic acid or of dicarboxylic acids e.g. adipic acid with polymethylene diamines by hexamethylene diamine, furthermore, polyacrylonitrile, polyesters for example of terephthalic acid and ethylene glycol, copolymers of vinylchloride and acrylonitrile and the like. Glass may also be used.

The atomizing effect occurs both with negative and positive electrodes, and it is thus possible, depending on the potential of these electrodes to produce negatively or positively charged liquid aerosols. For the development of charged images, the possibility is thus provided to produce a negative or positive visible image of the original.

The electrodes can for example have the form shown in the accompanying drawings. FIGURE 1 shows a plastic filament **3** which serves as a spray-type electrode and which is guided along a moistening cushion **5** by means of two guide rollers **4**, which consist of an electrically conducting material. This moistening cushion is impregnated with the dyestuff solution to be atmoized and continuously feeds the developing liquid to the electrodes. The reference numeral **1** designates an electrophotographic material and **2** represents a metallic support serving as counter-electrode.

If necessary, several plastic filaments arranged in juxtaposition can be used as electrodes.

FIGURE 2 shows another constructional form, in which a conductive band **6**, which is provided with bristles of

nonconductive material **7** and is guided by two guide rollers **8** of conductive material continuously through a dyestuff solution in a container **9**, the bristles serving as spray electrodes being supplied constantly with fresh developer liquid.

The use of several electrodes and the movement of the electrodes relatively to the photoconductor layer make it possible for images having relatively large areas to be developed, as described by way of example in French Patent No. 1,273,337.

Bell-shaped electrodes or nozzles and endless filaments can also be produced of metals. In this connection it is important that the metallic electrode is easily wettable by the developer liquid, since the surface of the portions of the electrode from which the developer is to be atomized have to be completely covered by the developer liquid.

For the continuous operation of a developing apparatus with electrostatic spray-type or atomizing electrodes which are used for the developing of large-area charging images, ant more especially for those having continuous tones, the atomizing electrode alone is generally not sufficient as a development electrode to produce sufficiently high contrasts and a satisfactory gradation of continuous tone images.

According to a preferred embodiment of the invention, which is shown in FIGURES 3–5, a simplified atomizing electrode **11** is used in combination with a grid electrode **12** for the image development (see FIG. 3). The atomizing electrode consists of a hollow cylinder **13**, which is enlarged funnel-shaped at one end and is provided with a sharp evenly formed rim. The tube-shaped electrode **11** is so secured in a holder **14** that its longitudinal axis is vertical and its funnel-shaped enlargement **15** is at the bottom end. This construction has the advantage that sufficient quantities of liquid can be sprayed with adequate fineness with a single electrode under positive potential of 10 to 40 kv., preferably about 20 kv. The dimensions are so chosen that the electric field intensity at the rim of the funnel is sufficiently large for positive atomization, and also to achieve constant wetting of the electrode rim, which is an essential condition for good atomization. The opening angle and the width of the funnel are kept sufficiently large for the internal space of the funnel to be partially filled with liquid in the operative condition, so that a coherent inwardly curved liquid surface **16** defined by the funnel rim is formed by the action of the surface tension. In this way, the uniform wetting of the electrode rim is made possible.

The following dimensions can for example be used for the electrode:

Length of the cylindrical portion (a)	20 to 100 mm.
Diameter of the cylindrical portion (b)	1 to 3 mm., advantageously 2 mm.
Internal diameter of the cylindrical (c) portion	0.3 to 2 mm., advantageously 1 mm.
Diameter of the funnel rim (d)	1 to 10 mm., advantageously 6 mm.
Opening angle (α)	20 to 100 degrees, advantageously 30 degree.

According to FIG. 4, the electrode is connected through a pipeline **17** to a pump **18** for a constant delivery of the liquid, the necessary quantity of coloring liquid being conveyed from a reservoir **19** to the atomizing electrode. The delivery output is adjustable and, depending on the capacity for atomization of the dye solution, is 0.001 to 0.5 cc./min. advantageously 0.15 cc./min. The pump can for example be constructed as a gear pump, which is driven by an adjustable gearing.

The atomizing electrode is fixed to a holding arm **14**, which can be moved by siutable guide mechanism in such a way that the electrode sweeps over the grid electrode **12** adjustably positioned above the photo-conducting layer at a height of 20 to 200 mm., advantageously 50 mm., so that the sprayed dye aerosol can be deposited on each part of the image with sufficient density and uniformity through the grid.

The operation of the apparatus according to the invention is shown more especially in FIGS. 4 and 5 which are hereinafter described.

The grid electrode **12** is in the form of a flat, conductive grid, which can be placed at a small distance above the photoconductive layer **20** which is charged to form an image, and thus it follows that it is charged with the same sign as the image. The grid has the following functions:

(1) The proportion of the dye aerosol which is not required for the image development, for example the dyestuff over the areas of the picture which remain white, are deposited electrostatically on the grid.

(2) The ion stream of positive ions, which is formed with the atomization of the dyestuff solution and which has a harmful effect on the image development, is for the major part taken up by the grid.

(3) The grid electrode screens the photoconductive layer from the electric field which is built up by the atomizing electrode which is under high voltage and simultaneously intensifies the graduated electric field produced in image formation over the charged image. By this means, the contrasts are brought out.

In order to control the image field for harder or softer development, the grid electrode **12** is connected to a direct voltage source **21** with an adjustable voltage in the range from −1000 to +500 volts. The mesh width of the grid, which must not be too small, because otherwise the openings are too quickly clogged by the deposited aerosol, but which also must not be too large, since otherwise the grid structure is projected in an undesirable manner on the image surface, can, with crossed grids, be upwards from 0.2 mm. to sizes which correspond approximately to the distance of the grid from the image plane. When the distance between the grid and image plane is adjustable in the range from 1 mm. to 20 mm., advantageously 5 mm., a crossed grid with a mesh width of 1 mm. is for example employed.

Because of constant deposition of the dyestuff solution on the grid, it is necessary to carry out cleaning at predetermined time intervals, preferably after developing each image. This is for example possible by using a grid arranged to pivot about a pivot axis **22** (as shown in FIG. 5, but omitted from FIG. 4 for the sake of clarity) in such a way that it can be swung from the horizontal position above the photoconductive layer and can be pressed against an absorbent, replaceable pad **23**, which absorbs the dyestuff.

Serving as a base for the photoconductive layer support is a grounded metal plate **24**, which is provided on two sides with guide rails **25**, in which the layer support can slide. The size of the support corresponds to the format of the copy. A cutting device **26** is arranged on one edge of the plate. The electrophotographic material, which consists for example of a paper support and a photoconductive layer of zinc oxide dispersed in silicone resin, is withdrawn from a reel **27** arranged behind the metal plate **24**. For taking the paper from the reel **27** and for feeding it into the guide rails **25**, a pair of rollers **28** is provided, as clearly shown in FIG. 5 and partially shown in FIG. 4, these rollers being arranged between the reel and metal plate and being coupled to an electrical drive means. For charging the layer, needle electrodes **29** are used, which are arranged to be movable above the image area.

By means of a program control mechanism, the following operational steps are succesively carried out in an automatic manner:

(1) Feeding in of the electrophotographic paper until the base is completely covered.

(2) Charging by the needle electrodes.

(3) Exposure of an image by a suitable optical system.

(4) Positioning of the grid on the layer being imagewisely charged and development by the atomizing electrode sweeping over the grid.

After completing the development, the grid is removed and pressed against the absorbent pad **23**. Simultaneously, the paper strip is advanced by the width of one sheet by the pair of rollers and the sheet on top with the colored image is cut by the cutting device **26**, so that the electrophotographic paper is used without waste. In this way, the starting position is again reached and the apparatus is ready for use for the making of the next copy.

The image development on a fixed sheet has the advantage, by comparison with a traveling strip, that a multicolor development can be carried out by repeated charging, light-exposure and development of one and the same layer. For this purpose, the simple pump **18** for dye liquid can be replaced by a multiple pump for different dye liquids. In this case it is advantageous to provide for each dye liquid an individual atomizing electrode so that colored partial images can be successively developed.

For the production of positive copies as intended by development of a charged image, only a positively charged aerosol is necessary, since for example only charged images with negative charging can be produced with advantage on zinc oxide-resin layers, which then provide a visible positive image of an original when developed with positive aerosol. By electrostatic atomization of liquids with an electrical conductivity in the practical range of 10^{-8} to 10^{-3} ohm^{-1} cm.$^{-1}$, it is found by experience that positively charged aerosols can be produced substantially more easily than negatively charged aerosols. This means, inter alia, that for the positive atomization. the electrode surface does not definitely have to be so strongly curved as for negative atomization, so that for positive atomization alone, a more simple form of electrode, e.g. a funnel-shaped electrode is possible.

Conductive images, which are for example prepared by the process disclosed in French Patent No. 1,244,027, can be developed directly as negative images if the photoconductor layer which is exposed to form an image is used with a grounded metallic support as counter-electrode. The process of the invention permits the reproduction of both line originals and continuous-tone images.

Suitable are especially liquids which have a permanent dipole moment and a conductivity of advantageously 10^{-3} to 10^{-8} Ω^{-1} cm.$^{-1}$. Strongly polar liquids of high conductivity, such as aqueous solutions and the like, as well as non-polar liquids, such as carbon tetrachloride, carbon disulphide, unsubstituted aromatic substances etc., cannot be used. A particularly fine atomization is possible when using alcohol, ethanol, and some acids, acid ester and halogenated hydrocarbons. Methanol, ethanol, propanol, butyl alcohol, amyl alcohol, benzyl alcohol, acetone, glacial acetic acid or ethylene chloride are specifically mentioned.

Aqueous systems of low surface tension having a suitable conductivity e.g. solutions or dispersions of a dye in aqueous alcohols can also be used. Especially useful is benzyl alcohol, which is an excellent medium for many dyestuffs and which, furthermore, is non-combustible and not too volatile.

As explained in the following table, there is a connection between the conductivity of the developer and the sign of the charging of the aerosol produced thereon. Thus, negative and positive aerosols can be produced from developers with a conductivity between 10^{-5} and 10^{-8} Ω^{-1} cm.$^{-1}$, while those which have a conductivity from 10^{-3} to 10^{-5} Ω^{-1} cm. can preferably be produced by means of a positive electrode.

Dyestuff (35 percent solution in benzyl alcohol)	Constitution	Conductivity in Ω^{-1} cm.$^{-1}$	Sign of the charging of the aerosol
Sirius Violett extra konz. BB	No. 27 905	$5 \cdot 10^{-6}$	Negative and positive.
Reflexblau 66 extra	Tri-m Tolyl-p-rosanilin-mono-sulpho acid.	$2.2 \cdot 10^{-5}$	Positive and negative.
Acilan Violett S 4 BN extra konz	No. 42 640 Color Index	$4.2 \cdot 10^{-5}$	Do.
Astra new Fuchsin konz	No. 782 Schultz 7th Edition	$3 \cdot 10^{-4}$	Positive.
Astra Blau 3R kochkonz	Friedl. XII/209	$3.7 \cdot 10^{-4}$	Do.
Kristallviolett extra neu	No. 785 Schultz 7th Edition	$8 \cdot 10^{-4}$	Do.

By the method according to the invention the dyestuffs can be both dissolved and dispersed in the liquid. The spraying effect is scarcely dependent on the nature of the dyestuff distribution. The following are mentioned as dyestuffs which can be used:

Sudanrot (No. 976), Sudan R (No. 149), Sudan III (No. 532), Sudan IV (No. 541), Sudan CB (No. 127), Sudan II (No. 92), Sudan I (No. 33), Sudan G (No. 31), Sudan-braun (No. 115), Nigrosin (No. 986), Parablau (No. 987), Brillantblau CC (No. 991), Nigrosinbase (No. 985).

The numbers in parentheses after the dyestuffs are the dyestuff numbers in Schultz, first volume, seventh edition. The following are also suitable: Benzinblau 1,4-di-isobutylamino anthraquinone and Ceresblau (color index vol. 3, No. 44, 065) and others.

Example 1

An electrophotographic material, consisting of a paper support, and a photoconductive layer consisting for example of photoconductive zinc oxide disposed in an insulating binder is charged in the usual manner and an electrostatic charging image is produced by image-wise exposure of the charged material.

This charged image is made visible with the aid of the arrangement shown in FIG. 2. The bristles of nylon used for the spray electrodes have a diameter of 0.2 mm. and a length of about 10 cm. The spacing of these electrodes from the electrophotographic layer is 30–50 mm.; the applied voltage is about 10 kv. A saturated solution of Ceres black in benzyl alcohol serves as developer liquid.

A satisfactory reproduction is obtained with uniformly covered surfaces.

Example 2

320 g. of silicone resin (for example type Bayer P 150), 60 percent in toluene, 500 g. of toluene and 450 g. of chemically pure, photoconducting zinc oxide are ground for about 3 hours in a ball mill, thereafter cast on to paper and dried. The electrophotographic paper thus produced is electrostatically charged by means of a corona discharge device and exposed through a continuous-tone original.

The exposed material is processed by means of a developing device shown in FIGURES 3–5. The aerosol was produced by atomizing an approximately 30 percent solution of Ceres blue in benzyl alcohol. The developer is sucked up by the photoconductive layer, so that no drying is necessary. An excellent reproduction of the original is obtained.

Similar results are obtained if dyestuff solutions in other organic solvents, for example n-butyl-benzoate are used.

All kinds of different electrophotographic materials can be processed in the developing apparatus as described above, for example those which are described in German Patents 1,090,093, 1,046,493, 1,031,127 and 1,052,811. Particularly suitable are the usual electrophotographic materials containing zinc oxide as a photoconductive substance, the said oxide being dispersed in an insulating binder.

What is claimed is:

1. A method of developing a latent electrostatic image carried by a photoconductive layer which comprises treating the photoconductive layer with an electrically charged liquid aerosol continuously generated and simultaneously charged during the development by electrostatic atomization of a liquid developer composed of a solution of at least one dyestuff in a solvent having an electrical conductivity of between 10^{-3} and 10^{-8} ohm^{-1} $cm.^{-1}$, said charged liquid aerosol being generated continuously during the development from strongly curved surfaces of an electrostatic atomizing electrode by the action of a strong non-homogenous electric field of the electrostatic atomizing electrode, the said charged liquid aerosol being projected through the oppositely charged conductive grid of an intermediate electrode, which is arranged parallel to and at a distance of between 1 and 20 mm. from the photoconductive layer and which grid has the same chage as the photoconductive layer, into the space between the photoconductive layer and the grid electrode whereby the charged liquid aerosol is deposited in accordance with a latent electrophotographic image onto the photoconductive layer, atomizing electrodes in the form of filaments of electrically non-conducting materials being used, the surface of the electrodes being made sufficiently conductive for the atomizing effect by continuously wetting with said developer liquid which is to be atomized.

2. A method of developing a latent electrostatic image carried by a photoconductive layer with an electrically charged liquid aerosol continuously generated and simultaneously charged during the development by electrostatic atomization of a liquid developer composed of a solution of at least one dyestuff in a solvent having an electrical conductivity of between 10^{-3} and 10^{-8} ohm^{-1} $cm.^{-1}$, said charged liquid aerosol being generated continuously during the development from strongly curved surfaces of an electrostatic atomizing electrode by the action of a strong non-homogenous electric field of the electrostatic atomizing electrode, the said charged liquid aerosol being projected through the oppositely charged conductive grid of an intermediate electrode, which is arranged parallel to and at a distance of between 1 and 20 mm. from the photoconductive layer and which grid has the same charge as the photoconductive layer, into the space between the photoconductive layer and the grid electrode whereby the charged liquid aerosol is deposited in accordance with a latent electrophotographic image onto the photoconductive layer, atomizing electrodes in the form of bristles of electrically non-conducting materials being used, the surface of the electrodes being made sufficiently conductive for the atomizing effect by continuously wetting with said developer liquid which is to be atomized.

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