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METHOD OF CYCLICALLY DEVELOPING ELECTROSTATIC LATENT IMAGES

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ABSTRACT OF THE DISCLOSURE

An electrostatographic imaging system wherein an electrostatic latent image is developed by placing the imaging surface in developing configuration with a patterned applicator surface having a substantially uniform distribution of raised portions or "lands" and depressed portions or "valleys" and containing a relatively non-conductive liquid developer in the depressed portions thereof while the raised portions are substantially free of developer.

CROSS REFERENCES TO RELATED APPLICATIONS

This application is a continuation application of U.S. Ser. No. 839,801, filed July 1, 1969, now abandoned.

BACKGROUND OF THE INVENTION

This invention relates to imaging systems, and more particularly, to improved developer systems and techniques.

The formation and development of images on the surface of photoconductive materials by electrostatic means is well known. The basic xerographic process, as taught by C. F. Carlson in U.S. Pat. 2,297,691 involves placing a uniform electrostatic charge on a photoconductive insulating layer, exposing the layer to a light-and-shadow image to dissipate the charge on the areas of the layer exposed to the light and developing the resulting electrostatic latent image by depositing on the image a finely-divided electroscopic material referred to in the art as "toner." The toner will normally be attracted to those areas of the layer which retain a charge, thereby forming a toner image corresponding to the electrostatic latent image. This powder image may then be transferred to a support surface such as paper. The transferred image may subsequently be permanently affixed to a support surface as by heat. Instead of latent image formation by uniformly charging the photoconductive layer and then exposing the layer to a light-and-shadow image, one may form the latent image directly by charging the layer in image configuration. The powder image may be fixed to the photoconductive layer if elimination of the powder image transfer step is desired. Other suitable fixing means such as solvent or overcoating treatment may be substituted for the foregoing heat fixing step.

Similar methods are known for applying the electroscopic particles to the electrostatic latent image to be developed. Included within this group are the "cascade" development technique disclosed by E. N. Wise in U.S. Pat. 2,618,552; the "powder cloud" technique disclosed by C. F. Carlson in U.S. Pat. 2,221,776 and the "magnetic brush" process disclosed, for example, in U.S. Pat. 2,874,-063

Development of an electrostatic latent image may also be achieved with liquid rather than dry developer materials. In conventional liquid development, more commonly referred to as electrophoretic development, an insulating liquid vehicle having finely divided solid material dispersed therein contacts the imaging surface in both charged

and uncharged areas. Under the influence of the electric field associated with the charged image pattern the suspended particles migrate toward the charged portions of the imaging surface separating out of the insulating liquid. This electrophoretic migration of charged particles results in the deposition of the charged particles on the imaging surface in image configuration. Electrophoretic development of an electrostatic latent image may for example, be obtained by flowing the developer over the image bearing surface, by immersing the imaging surface in a pool of the developer or by presenting the liquid developer on a smooth surfaced roller and moving the roller against the imaging surface.

A further technique for developing electrostatic latent images is the liquid development process disclosed by R. W. Gundlach in U.S. Patent 3,084,043 hereinafter referred to as polar liquid development. In this method, an electrostatic latent image is developed or made visible by presenting to the imaging surface a liquid developer on the surface of a developer dispensing member having a plurality of raised portions or "lands" defining a substantially regular patterned surface and a plurality of portions depressed below the raised portions or "valleys." The depressed portions of the developer dispensing member contain a layer of conductive liquid developer which is maintained out of contact with the electrostatographic imaging surface. Development is achieved by moving the developer dispensing member loaded with liquid developer in the depressed portions into developing configuration with the imaging surface. The liquid developer is believed to be attracted from the depressed portions of the applicator surface in the charged or image areas only. The developer liquid may be pigmented or dyed. The development system disclosed in U.S. Patent 3,084,043, differs from electrophoretic development systems where substantial contact between the liquid developer and both the charged and uncharged areas of an electrostatic latent imaging surface occurs. Unlike electrophoretic development systems, substantial contact between the polar liquid and the areas of the electrostatic latent image bearing surface not to be developed is prevented in the polar liquid development technique. Reduced contact between a liquid developer and the non-image areas of the surface to be developed is desirable because the formation of background deposits is thereby inhibited. Another characteristic which distinguishes the polar liquid development technique from electrophoretic development is the fact that the liquid phase of a polar developer actually takes part in the development of a surface. The liquid phase in electrophoretic developers functions only as a carrier medium for developer particles.

While capable of producing satisfactory images these liquid development systems in general suffer deficiencies in certain areas and are in need of further development and improvement. Particularly troublesome difficulties are encountered in liquid development systems employing a reusable or cycling electrostatographic imaging surface. In these systems an imaging surface such as a selenium or selenium alloy drum type photoconductor is charged, exposed to a light and shadow image and developed by bringing the image bearing surface into developing configuration with an applicator containing developing quantities of liquid developer thereon. The liquid developer is transferred according to the appropriate technique from the developer applicator onto the image bearing surface in image configuration. Thereafter, the developer pattern is transferred to a receiving surface such as paper. During the transfer step not all the liquid developer is transferred and therefore a subsequent cleaning step is required.

In electrophoretic development the entire imaging surface is contacted with the liquid developer with the charged

particles separating from the carrier liquid and migrating to the charged field or image portions. The particles strongly adhere to the imaging surface by means of van der Waals forces since the particles frequently come within about five hundred angstroms of the imaging surface. The van der Waals forces are so strong that in the subsequent transfer step a considerable portion of the particles remain on the imaging surface thus producing prints of relatively low density. In addition to poor density with transfer, the adhering particles on the imaging surface drastically increase the effort necessary to clean the residual developer from the imaging surface and frequently require sufficient cleaning to result in degradation of the photoconductor. In general, electrophoretic development in systems employing recycling electrostatographic imaging surfaces provides low efficiency in both transfer of the developer to a reeciving surface and in the cleaning step. Further more, since there is a general area contact by the liquid portion of the developer with the entire imaging surface some of the liquid vehicle will be present in the background areas of the final copy. When the liquid vehicle is a volatile vehicle some heat must generally be supplied to evaporate the layer of vehicle in the background areas. On the other hand, non-volatile liquids generally produce prints with oily or greasy background areas. In either case, without a heating or fusing step the copy paper is usually wet and the image area poorly fixed to the copy paper. Furthermore, the developers used in electrophoretic development are polarity sensitive. That is, they must be specially selected to develop images of either positive or negative charge. In addition, in electrophoretic development there may be a gradual depletion of electroscopic particles in the developer since they separate from the carrier liquid during development. Any depletion may be significant since generally only relatively small quantities of electroscopic particles are present in the developer to ensure low viscosity of the liquid developer necessary for acceptable development speeds.

In the polar ink development systems disclosed in U.S. Pat. 3,084,043 the developing liquid is relatively conductive having a resistivity less than 10^{10} ohm centimeters. After transfer of the developer in image configuration from the electrostatographic imaging surface to a receiving surface and even relatively vigorous cleaning, a portion of this type of developer is also observed to remain on the imaging surface. This developer residue is damaging to cyclical use of the imaging surface. Subsequent recharging of the photoconductor, for example, may be inadequate since the conductive liquid may dissipate the charge. Furthermore lateral conductivity of the liquid developer on the photoconductor may become excessive and the resolution of the resulting image will be poor.

In many of the developer materials employed in these techniques hyperoscopic developer materials are employed which absorb atmospheric moisture thereby lowering the developer viscosity and altering the developing conditions. It is, therefore, clear that there is a continuing need for a better liquid development system employing a cycling or reusable photoconductor.

SUMMARY OF THE INVENTION

It is, therefore, an object of this invention to provide a developing system which overcomes the above noted deficiencies.

It is another object of this invention to provide a liquid development system employing an electrostatographic imaging surface capable of repeated recycling.

It is another object of this invention to provide a liquid development system employing a cycling electrostatographic imaging surface permitting relative ease in cleaning.

It is another object of this invention to provide a liquid development system employing a reusable electrostatographic imaging surface wherein prints of improved resolution and/or density are obtained.

It is another object of this invention to provide a liquid development system which enables an electrostatographic imaging surface to be cycled repeatedly.

It is another object of this invention to provide a liquid development system employing a photoconductor capable of repeated cycling with incomplete cleaning of the photoconductor on each cycle.

It is another object of this invention to provide an electrostatographic imaging system employing a non-volatile liquid developer which produces prints which are not wet, slippery or greasy in the background areas.

It is another object of this invention to provide an electrostatographic imaging system employing liquid developers which are not polarity sensitive and which are stable suspensions independent of particle surface potential or concentration.

It is another object of this invention to provide liquid developers having high pigment contents.

It is another object of this invention to provide a liquid development system superior to known systems.

The above objects and others are accomplished, generally speaking, by providing an electrostatographic imaging system wherein an electrostatic latent image is developed by placing the imaging surface in developing configuration with a patterned applicator surface having a substantially uniform distribution of raised portions or "lands" and depressed portions or "valleys" and containing a relatively electrically non-conductive liquid developer in the depressed portions thereof while the surfaces of the raised portions are substantially free of developer.

Development is obtained by placing the applicator surface sufficiently close to the electrostatographic imaging surface such that the relatively non-conductive liquid developer is pulled from the recessed portions of the applicator surface to the imaging surface in image configuration. Generally to provide maximum image density it is preferred to place the raised portions of the applicator surface in slight or gentle contact with the imaging surface provided that the raised portions are substantially free of liquid developer.

Any suitable applicator surface may be employed which has a substantially uniform pattern of raised portions and depressed portion provided that the depressed portions are sufficiently large to hold developing quantities of liquid developer therein. To minimize wear on the imaging surface it is preferred to provide raised portions which are uniformly curved or substantially flat on the surfaces which contact the imaging surface.

Typical applicator surfaces include, among others, porous ceramics, metallic sponge, patterned webs or belts, capillary combs, and cylindrical rolls having surface patterns such as single screw cuts or trihelicoid, pyramidal or quadragravure indentations. To provide good image resolution it is preferred that the applicator surface have a pattern comprising between about 100 and about 300 demarcations of raised or depressed areas per inch. Generally, with more coarse patterns, insufficient resolution is obtained and with finer patterns insufficient loading of developer in the recessed portions is obtained to provide good image density. It is generally preferred to employ a pattern of recessed grooves such as in the trihelicoid pattern since this pattern facilitates better doctoring of the applicator surface.

The applicator surface may be loaded with developer in any suitable manner. Typical developer loading techniques include applying developer from a roll or sponge roll or immersing the applicator in a bath. Prior to contacting the imaging surface, the applicator surface should be wiped or "doctored" clean to remove substantially all liquid developer from the raised portions of the applicator surface. Any suitable means may be provided as the doctoring device. Typical doctoring devices include scraper blades and squeegee rolls. The doctoring in addition to removing liquid developer from the raised portions of the applicator surface preferably provides a slight wiping action of

the liquid developer in the recessed portions of the applicator surface to thereby maintain the level of the liquid developer in the recessed portions slightly below the level of the raised portions. Such a loading of developer on the applicator surface minimizes deposits in the non-image areas.

Any suitable liquid developer composition may be employed which is relatively electrically non-conductive. Typically, the developer has a bulk resistivity greater than 10^{10} ohm centimeters and less than about 10^{15} ohm centimeters. In recycling systems, the more electrically conductive the developer, the greater the opportunity for decreased charge retention and increased lateral conductivity on the imaging surface and therefore poor resolution. On the other hand, the more electrically resistive the developer is, the greater the time constant for lateral discharge of the image. Lateral discharge is of significance in a recycling system since for each imaging cycle there is generally a residue of developer remaining on the imaging surface from the preceding cycle and placing of the charged image on the imaging surface must take place with the residual developer still on it.

The time constant τ_s for the lateral discharge of the smallest image element "i" to be resolved to its surroundings is determined by the well known relationship. $\tau_s=\rho {}^{c}i/d$, where ρ and d are respectively the bulk resistivity and thickness of the residual liquid developer film and ${}^{c}i$ the capacitance of area element i of the dielectric or photoconductor. For a resolution of 10 lp./mm., the area of element i is 10^{-4} cm.^{2}. For a typical 50μ selenium photoconductor layer of dielectric constant $\epsilon=6$, or a typical 25μ organic dielectric of $e=3$, ${}^{c}i\approx 10^{-14}$ farad/element. With a typical liquid developer film residue of the order of 1.0μ or 10^{-4} cm. in thickness, $\tau_s\approx 10^{-10}\rho$ sec. Therefore the time for $1-1/\rho$ (or 63%) discharge of an image element by lateral conduction through the liquid residue film is given by Table 1:

TABLE 1

ρ, ohm cm.	τ_s, sec.
10^{10}	1.0
10^{11}	10
10^{12}	100
10^{13}	1000
10^{14}	10^4

Since at the present state of the art, practical electrostatic imaging rates require a latent image life of the order of at least about 1 sec., and preferably 2 or 5 sec., it follows that liquid developers for practical cycling photoreceptors should have a resistivity of at least 10^{10} ohm cm. as measured by conventional pulsed D.C. parallel plate conductivity cell method.

The rate of development is set by a similar time constant, but one which involves the rate of charge induction through the liquid developer: $\tau_1\approx\epsilon_0\epsilon_1\rho$ where ϵ_1 is the dielectric constant of the liquid, ϵ_0 the permitivity of free space (8.85×10^{-14} fd./cm.) and ρ the resistivity of the liquid, as before. Values of ϵ_1 range generally from 2 to 6, with 3.4 a typical example, applicable to many mineral oil based liquid developers. Assuming an effective developing zone about 0.2 inch in width, the electrical limitation or maximal development speed may be estimated as: $v_{max}=0.20/\tau_1$ (inches/sec.).

TABLE 2

ρ	10^{10}	10^{11}	10^{12}	10^{13}	10^{14}	Ohm cm.
τ_1	3.0	30	300	3,000	30,000	Millisec.
v_{max}	66	6.6	.66	.066	.0066	Inches/sec.

This theory indicates that high development rates may be achieved at $\rho<10^{11}$ ohm cm. However, actual experience indicates that it does not predict the limiting velocities at $\rho>10^{12}$ ohm cm. very accurately. Instead, some additional mechanism which is not yet clearly understood provides a maximal development speed greater than about 3 inches/sec. even at $\rho=10^{13}$–10^{14} ohm cm. It follows that liquid developers are operable in the entire resistivity range cited (10^{10}–10^{14} ohm cm.). The preferred and most practical operating range of resistivity providing the balance between conductivity, time constant and development speed is from about 2×10^{10} to about 10^{12} ohm cm.

An optimum balance between conductivity and time constant is generally obtained with developers having a resistivity of from about 10^{11} to about 10^{12} ohm centimeters.

The developers of this invention may include one or more liquid vehicles, colorants such as pigments and dyes, and dispersants. In addition, a variety of specialized agents may be employed for particular functions. For example, viscosity controlling additives or additives which contribute to fixing a pigment on copy paper may be employed.

Any suitable vehicle contributing to the above properties may be used. Typical vehicles within this group that may be employed singly or in combination include mineral oil, vegetable oils, such as castor oil and its oxidized derivatives, peanut oil, coconut oil, sunflower seed oil, corn oil, rape seed oil, and sesame oil. Also included are mineral spirits, fluorocarbon oils such as du Pont's Freon solvents and Krytox oils, silicone oils, kerosene, carbon tetrachloride, toluene, oleic acid and drying oils such as linseed oil and tung oil and highly purified polypropylene glycol.

In addition to the above vehicles an auxiliary or secondary vehicle may be employed to impart or adjust any one or more of the properties of the liquid developer. Any suitable material may be employed as the secondary vehicle and may, for example, have dispersant properties, contribute to viscosity adjustment, or confer wetting properties to the pigment employed or act as a fixing agent. In addition, the secondary vehicles preferably exhibit properties in common with the principal vehicle of being non-odorous, non-hygroscopic, and of low volatility to provide a stable developer with a non-offensive odor. An additional function of secondary vehicles may be to help the developer penetrate into the copy paper. Typical materials that may be employed as secondary or primary vehicles include dibutyl phthalate, butyl isodecyl phthalate, butyl octyl phthalate, diisooctyl phthalate, di(2-ethyl hexyl) phthalate, isooctyl isodecyl phthalate, normal octyl decyl phthalate, diisodecyl phthalate, ditridecyl phthalate, isodecyl tridecyl phthalate, diisooctyl adipate, di(2-ethyl hexyl) adipate, isooctyl iosdecyl adipate, normal octyl decyl adipate, diisodecyl adipate, diisooctyl sebacate, di 2-ethyl hexyl sebacate, polyadipate ester, polyadipate ester, isooctyl palmitate, butyl stearate, butyl oleate, triethylene glycol dicaprylate, triethylene glycol caprylate-caprate, triethylene glycol dipelargonate, diethylene glycol dipelargonate, butanedial dicaprylate, triisooctyl trimellitate, tri 2-ethyl hexyl trimellitate and mixed normal trialkyl trimellitates.

Any suitable colorant may be employed in the developer including both pigments and dyes. It is preferred that the colorant be fast to light in order to obtain image permanence. Typical pigments include carbon black, charcoal and other forms of finely-divided carbon, quinacridones, phthalocyanine blues, iron oxide, ultramarine blue, zinc oxide, titanium dioxide, and benzidine yellow. Typical dyes include Irgacet Black RL., oil red, oil blue, oil yellow. Because of the relative ease in being dispersed throughout the vehicle surface resinated pigments such as those manufactured by CIBA under the tradename "Microlith" are preferred. Microlith CT is a preferred resinated carbon black. While dyes may be employed it is generally preferred to employ pigmented developers since they provide better archival permanence, are more readily immobilized at the point of deposition and provide higher density since they tend to be filtered out and remain closer to the paper surface on the final print.

A dispersant is generally employed to aid in dispersing the pigment and other additives in the vehicles. Any suitable dispersant may be employed that is compatible with and soluble in the vehicle, Typical materials include alkylated polyvinyl pyrrolidone and wood rosin derivatives such as Stabelite ester, manufactured by Hercules Powder Co. and interpolymers of n-octodecyl vinyl ether and maleic anhydride such as Gantrez AN 8194 manufactured by GAF Corp.

The proportions of the several constituents in the developer may be varied over a wide range depending on individual properties of the constituents and operational considerations of the specific development scheme. A significant factor in determining proportions is the speed of development since with higher speeds lower viscosity developers must be used than at lower speed. One skilled in the art may readily determine the appropriate viscosity for any given development speed.

In liquid development systems having development speeds of from about 5 to about 20 inches per second, for example, developer viscosities of from about 300 to about 1800 centipoises measured at 25° C. are preferred to provide ease of operation and desired print quality. Speeds of 200 inches per second, on the other hand, require a lower viscosity, typically of the order of about 100 centipoises. The viscosity is in part dependent on the pigment loading of the vehicle. At constant dispersant concentration as more pigment is added the viscosity of the developer increases and operable development speed is lowered. The balance between pigment loading and dispersant concentration to obtain maximum image density and development speed to maintain maximum development may be readily determined by one skilled in the art.

The several constituents may generally be present in a developer in amounts according to the following weight percentages:

	Wt. percent
Vehicle (including principal and secondary vehicle	From about 40 to about 90
Colorant: Pigment or dye	Up to about 60
Dispersants	Up to about 20

Typical developers have the following composition by weight:

	Wt. percent
Total vehicle	From about 40 to about 85
Colorant: Pigment or dye	From about 15 to about 60
Dispersants	From about 1 to about 20

Within the broad range of proportions set forth above a preferred range of proportions for the constituents of the developer providing good print quality and ease of operation are the following:

	Wt. percent
Total vehicle	From about 65 to about 85
Primary vehicle	From about 20 to about 85
Secondary vehicle	From about 0 to about 45
Colorant	From about 20 to about 50
Dispersant	From about 5 to about 15

Particularly preferred formulations in providing optimum image density and resolution include a pigment loading of from about 30% to about 40% by weight.

The developers of this invention may be prepared by simply mixing the several constituents. However, to provide homogeneity it is generally preferred to combine the constituents of the vehicle first while heating them and then adding dispersant, pigment or dye any any other additives. The pigment may be comminuted separately or together with the vehicle. In addition, suitable control, suspending and fixing agents as are well known in the art may be added in conventional manner.

Developmet of an electrostatic latent image according to the technique described herein may be obtained on any suitable electrostatographic imaging surface. Basically, any surface upon which an electrostatic charge pattern may be formed or developed may be employed. Typical electrostatographic imaging surfaces include dielectrics such as plastic coated papers, xeroprinting masters, and photoconductors. Typical photoconductors that may be employed include selenium and selenium alloys, cadmium sulfide, cadmium sulfo selenide, phthalocyanine binder coatings and polyvinyl carbazole sensitized with 2,4,7-trinitrofluorenone. The electrostatographic imaging surface may be employed in any suitable structure including plates, belts or drums and may be employed in the form of a binder layer coated on a substrate. The imaging surfaces may be overcoated with suitable dielectric materials in conventional manner.

In the cycling electrostatographic imaging systems of the present invention it is generally necessary to cyclically clean the imaging surface. Any suitable cleaning system may be employed. A typical cleaning system scrubs the ink film on the photoconductor surface obliterating the image pattern by smearing the developer over the surface. The residual developer is subsequently picked up by an absorbent web which may absorb the developer. For example, a squeegee roller may be used as the scrubbing or obliterating device and an absorbent web wrapped around a portion of the photoconductor drum and moving slowly counter to the direction of rotation of the drum may be used.

The mechanism of development according to this invention is presently believed to be substantially the same as that in the polar ink development technique described by R. W. Gundlach in U.S. Pat. 3,084,043. The liquid developer is applied to the patterned applicator such that the raised portions of the applicator surface are substantially free of developer and the level of liquid in the recessed portions of the applicator is slightly below the level of the lands. Surface tension retains the developer in cohesive configuration in the depressed portion of the applicator surface and as the raised portions of the applicator surface are placed in light or gentle contact with the electrostatographic imaging surface the liquid developer in response to the electrostatic field of force on the imaging surface creeps up the sides of the depressed portions of the applicator surface and deposits on the imaging surface substantially only in accordance with the pattern of electric charge. The developer remains in the depressed portions of the applicator surface except in those portions which are under the influence of the attracting electrostatic force.

The developer applicator is generally biased or directly connected to ground through connection to a variable D.C. potential source so that the liquid developer will be electrostatically attracted from the applicator to the imaging surface in image configuration. When so biased, the charges on the imaging surface induce equal and opposite charges in the liquid developer. For example, when the applicator is grounded and the image surface carries a positive charge, negative charge is induced in the liquid developer adjacent the positive charges and the developer moves toward the imaging surface in response to the electrostatic field generated between these charges. Portions of the imaging surface carrying no charge, induce no charge in the developer and thus the developer is not pulled out of the recessed portions of the applicator surface to non-field areas of the image surface.

Reversal development may be obtained by applying to the developer applicator a potential of the same polarity and of the same amount as the charged areas on the imging surface to cancel out the field at charged areas and provide an electrostatic field between the uncharged areas of the imaging surface and the developer on the applicator surface. Again a charge is induced in the developer in response to the electrostatic field and the developer creeps up the recessed portions of the ap-

plicator surface adjacent areas of the imaging surface which are uncharged.

This is substantially the mechanism of development despite the fact that the developer is relatively non-conductive. The developers employed in this development mechanism are not polarity sensitive. That is, unlike classical electrophoretic developers, they are equally effective in developing positively, as well as negatively charged patterns on the imaging surface, the difference being only in the polarity of charge induced in the developer. Further, unlike electrophoretic development, migration of charged particles from the insulating carrier liquid plays no significant role. Instead, charge is induced in the entire developer which migrates substantially intact from the depressed portions of the applicator surface to the imaging surface. While particle migration may not be totally inhibited, if present, it is present in an insignificant insubstantial amount. This mechanism is generally substantiated by the fact that in development according to the disclosed technique the liquid developer is readily transferred and cleaned from the imaging surface and there is no evidence of the deposition of pigment particles out of the developer on the imaging surface. The additional observation that the developed image obtained according to the instant technique comprises both pigment particles and carrier liquid in substantially the same relative proportions as present in the original developer supply whereas a developed image obtained through electrophoretic development comprises substantially only the solid particles which have separated from the carrier liquid is further evidence of the differences between conventional liquid development and the described improved development technique.

DESCRIPTION OF PREFERRED EMBODIMENTS

The following preferred nonlimiting examples further define, describe and compare preferred materials, methods and techniques of the present invention: Examples III, IV, and VI are included for comparative purposes to show the surprisingly superior and unexpected results obtained in the practice of this invention. In the examples all parts and percentages are by weight unless otherwise specified.

Example I

The liquid developer employed in this example is of the following composition by weight and has a bulk resistivity of about 1.5×10^{10} (ohm cm.) and a dielectric constant of about 3.20.

	Parts
Drakeol 9	30
Ganex V216	15
Microlith CT	18
Methyl violet tannate	3
Paraffint RG wax	0.5

Drakeol 9 is a light mineral oil manufactured by Pennsylvania Refining Co. Ganex V216 is an alkylated polyvinyl pyrrolidone compound manufactured by GAF which serves as a pigment dispersant and may also be regarded as a vehicle. Microlith CT is a resinated pre-dispersed carbon black pigment composed of about 40% carbon black pigment and 60% ester gum resin manufactured by CIBA. Paraffint RG is a hard synthetic wax available in flake form from Moore and Munger.

The developer is prepared by combining the mineral oil and Ganex V216 in a suitable vessel while stirring, heating to about 100° C. and then adding the pigment and other ingredients while continuing the stirring.

The developer is applied to a cylindrical applicator roller having a trihelicoid pattern of about 150 lines per inch cut at an angle of about 45° to the longitudinal axis and to a depth of about 2.5 mils. The ridges of the applicator surface are substantially flat and the roller is wiped with a polyurethane doctor blade having a Shore A hardness of 85 durometers to remove substantially all developer from the ridges and provide a level of developer in the grooves slightly below the level of the ridges.

An electrostatic latent image is formed on a clean selenium xerographic plate comprising a surface layer of selenium about 50 microns thick on a conductive aluminum plate in conventional manner and the image is developed by moving the applicator roller over the selenium plate at a speed of about 10 inches per second, such that the edges are just in contact with the surface of the plate. A clearly defined developed image is observed on the selenium plate. The developer is transferred to bond paper in image configuration. The resolution of the print obtained is about 10 line pairs per millimeter and image density is 1.0 with background less than 0.01.

Example II

The procedure of Example I is repeated except that after the first print is obtained the selenium plate is manually cleaned with a cotton cloth to remove substantially all the residual developer. Thereafter, the selenium plate is charged, exposed, developed and the developed image transferred to paper in the same manner as in Example I. This sequence is repeated for 15 cycles. The resolution of the prints obtained is observed to gradually decrease from about 10 line pairs per millimeter on the first print to 8 l.p./mm. for the second, 4 l.p./mm. for the fourth, 3 l.p./mm. for the tenth and 1 l.p./mm. for the fifteenth. Image density remains nearly constant at about 1.0 with background at about 0.01 for all prints.

Example III

The procedure of Example I is repeated except that the developer is applied by totally immersing the selenium plate in a bath of developer. No image is developed on the plate. The plate is uniformly coated with developer.

Example IV

The procedure of Example I is repeated with a developer having the following composition by weight and having an electrical conductivity of about 1.4×10^{-7} $(\text{ohm cm.})^{-1}$ and a dielectric constant of about 39.5.

	Parts
Glycerol (USP grade)	61
Sorbitol	24
Triethanolamine	6
Santicizer 160	7
Methylene blue	1

Santicizer 160 is butylbenzyl phthalate manufactured by Monsanto.

The transferred print obtained on bond paper has good image density and resolution of about 5 line pairs per millimeter. The ink residue remaining on the selenium photoreceptor is substantially removed by rubbing the plate surface with absorbent cotton but still leaving a thin layer of ink film on the plate surface. The plate is now re-charged, exposed and passed through the developer as in Example I. No image is developed on the plate. The plate is now thoroughly cleaned of all ink film residue using soap and water and drying the plate by forced air drying for about one hour at 90° F. The plate is again charged, exposed and developed. The image now obtained on bond paper has good density and a resolution of about 3 line pairs per millimeter.

Example V

A paper backed zinc oxide binder layer photoconductor is charged and exposed in conventional manner. The electrostatic latent image is developed with a developer having the following composition by weight.

	Parts
Drakeol 9	38
Microlith CT	38
Rucoflex TG–8	9
Ganex V216	14

Drakeol 9 is a mineral oil manufactured by Pennsylvania Refining having a kinematic viscosity of about 15.7–18.1 centistokes at 25° C. and a specific gravity of 0.84. Rucoflex TG–8 is triethylene glycol dicaprylate manufactured by Hooker Chemical Company which serves as a solvent for the resinated carbon black pigment and may be regarded as a secondary vehicle in this formulation. The liquid developer has an electrical resistivity of about 0.7×10^{11} ohm cm. and is applied to the patterned applicator roll in the manner described in Example I. Development is obtained in the manner of Example I. The resolution of the developed image is observed to be about 8 line pairs per millimeter with good image density. The background areas of the zinc oxide paper are dry and not oily.

Example VI

The procedure of Example V is repeated except that the zinc oxide paper bearing the electrostatic latent image is immersed in the liquid developer. No image is developed on the paper. The zinc oxide paper is uniformly coated with developer.

Example VII

The procedure of Example I is repeated with a developer having the following composition by weight and having an electrical conductivity of about 3×10^{-14} (ohm cm.)$^{-1}$ and a dielectric constant of about 2.2.

	Parts
Oleic acid (USP grade)	75
Light resistant molybdate orange deep	25

Light resistant molybdate orange deep is a flushed predispersed pigment composed of about 75% pigment, 22% of a medium oil soya alkyd varnish and 3% mineral spirits manufactured by the Sherwin-Williams Co.

The transferred print obtained on bond paper has good image density and resolution of about 5 line pairs per millimeter. The selenium plate is cleaned as described in Example II and thereafter charged, exposed and developed for several cycles. After 10 cycles the resolution of the print obtained is 3 line pairs per millimeter.

Example VIII

A xeroprinting master is prepared by placing a thin insulating coating of epoxy resin about 0.0005 inch thick in image configuration on conductive plate of aluminum. The plate is charged to +450 volts by passing it under a corona charging unit. The image is developed with the liquid developer and in the manner described in Example I. The developer is transferred to bond paper and the resulting print has image density of about 1.1, background density of 0.01, and a resolution of about 5 line pairs per millimeter. The plate is cleaned as described in Example II. Thereafter, the xeroprinting master is repeatedly charged, developed and the developer transferred to bond paper as described above for 25 cycles. The speed of development is about 12 inches per second and the 25th print obtained is of substantially the same quality as the first print.

Example IX

Example VIII is repeated except that the xeroprinting master is replaced by a photoconductor comprising a 20 micron layer of selenium on an aluminum substrate overcoated with a quarter mil film of polyethylene terephthalate (obtained from E. I. du Pont de Nemours & Co. under the trade name Mylar) made according to the technique described in Example I of U.S. Pat. 3,251,686. Results similar to those obtained in Example VIII are observed on repeated cycling.

Examples I, II and VIII demonstrate the cycling ability obtained when employing the liquid developers and techniques of the invention. Print resolution of 5 line pairs per millimeter is generally recognized as very acceptable quality. Examples III and VI demonstrate that development according to a conventional electrophoretic development technique is not possible with the specified compositions. Example IV demonstrates that with a fairly conductive liquid developer recycling is impossible. The presence of the conductive developer residue on the imaging surface permits lateral discharge during charging and exposure to such an extent that there is a complete loss of resolution. Examples V and VI demonstrate that development with materials of very high pigment loading is possible according to the technique of this invention and not possible according to a conventional electrophoretic technique. In the xeroprinting mode of Example VIII since the image is the same for each cycle the cleaning step may be dispensed with.

As may also be observed from the foregoing description, examples and embodiments the materials and techniques of the instant invention have several advantages over known development systems. Development with a liquid developer may be obtained in a system employing a reusable photoconductor or other reusable electrostatographic imaging surface. The instant invention makes available as developers an additional group of nonvolatile materials and permits rapid development without a drying or heat fixing step. Unlike conventional electrophoretic development the background areas on the copy prints are not in contact with the developer and therefore remain dry and nongreasy and do not require a fusing step to fix the developer to the copy print. Further, since there is substantially no particle migration the composition of the developer in a developer supply does not have to be frequently monitored and adjusted and the developer image is not as closely held to the imaging surface, and, therefore, more readily transferred to a copy print and more readily cleaned.

Although specific materials and operational techniques are set forth in the above exemplary embodiments using the developer composition and development techniques of this invention these are merely intended as illustrations of the present invention. There are other developer materials and techniques such as those listed above which may be substituted for those in examples with similar results.

Other modifications of the present invention will occur to those skilled in the art upon a reading of the present disclosure which modifications are intended to be included within the scope of this invention.

What is claimed is:

1. The method of cyclically developing electrostatic latent image present on a reusable electrostatographic imaging surface comprising the steps of forming an electrostatic latent image on said reusable imaging surface, providing an applicator having a substantially uniform pattern of raised portions and depressed portions, said depressed portions containing developing quantities of an electrically non-conductive liquid developer having a bulk resistivity of from about 10^{10} ohm-cm. to about 10^{14} ohm-cm. while said raised portions are substantially free of liquid developer, positioning said applicator adjacent said imaging surface so as to induce equal and opposite charges in the liquid developer in regions corresponding to those areas of the imaging surface intended to be developed, such that the liquid developer is electrostatically pulled from the applicator to the imaging surface in image configuration, transferring said liquid developer from said imaging surface to a receiving surface, preparing said reusable imaging surface for the next imaging sequence and repeating the steps of forming, providing, positioning and transferring at least one additional time whereby residues of said non-conductive liq-

uid developer remaining on the imaging surface are not damaging to cyclical use of the imaging surface.

2. The method of claim 1 wherein said applicator is electrically biased.

3. The method of claim 1 wherein the electrostatographic imaging surface is a substrate backed photoconductive insulating binder layer.

4. The method of claim 1 wherein the electrostatographic imaging surface is a paper backed dielectric layer.

5. The method of claim 1 wherein the electrostatographic imaging surface comprises a photoconductor seselected from selenium or selenium alloys.

6. The method of claim 1 wherein the electrostatographic imaging surface is a xeroprinting master.

7. The method of claim 1 wherein the electrostatographic imaging surface is a phthalocyanine binder layer.

8. The method of claim 1 wherein the liquid developer has an electrical resistivity of from about 2×10^{10} ohm centimeters to about 10^{12} ohm centimeters.

9. The method of claim 1 wherein the liquid developer has an electrical resistivity of from about 10^{11} ohm centimeters to about 10^{12} ohm centimeters.

10. The method of claim 1 wherein said liquid developer is non-volatile.

11. The method of claim 1 wherein the developer during said positioning is substantially free of particle separation.

12. The method of claim 1 wherein pigment is present in the developer in an amount of from about 15 percent to about 60 percent by weight of the entire developer composition.

13. The method of claim 1 wherein pigment is present in the developer in an amount of from about 20 percent to about 50 percent by weight of the entire developer composition.

14. The method of claim 1 wherein pigment is present in the developer in an amount of from about 30 percent to about 40 percent by weight of the entire developer composition.

15. The method of claim 1 wherein the non-conductive liquid developer remains substantially homogeneous in composition throughout the several stages of development until it is transferred to the final receiver sheet.

16. The method of claim 1 wherein the applicator surface has a pattern of from about 100 to about 300 demarcations per inch.

17. The method of claim 1 wherein the applicator surface comprises a pattern cylindrical roll.

18. The method of claim 17 wherein the pattern is a trihelicoid pattern.

19. The method of claim 17 wherein the pattern is a single spiral groove pattern.

20. The method of claim 1 wherein a potential of the same amount and polarity as that of the charged areas of the imaging surface is applied to the applicator.

21. The method of claim 1 wherein the electrostatographic imaging surface is a dielectric overcoated photoconductor.

22. The method of claim 1 wherein the electrostatographic imaging surface is zinc oxide.

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