United States Patent

Amidon et al.

[15] 3,652,319

[45] Mar. 28, 1972

[54] CYCLIC IMAGING SYSTEM

[72] Inventors: **Alan B. Amidon; Joseph Mammino,** Penfield, N.Y.

[73] Assignee: **Xerox Corporation,** Rochester, N.Y.

[22] Filed: **Dec. 30, 1969**

[21] Appl. No.: **889,273**

[52] **U.S. Cl.** .....**117/37 LE,** 96/1, 96/1.4, 96/1.5, 134/1, 134/4, 134/5

[51] **Int. Cl.**.....**B05c 3/20,** B44d 1/02, B44d 1/52

[58] **Field of Search**.....96/1, 1.4; 134/1, 4, 5, 7; 117/37 LE

[56] **References Cited**

UNITED STATES PATENTS

3,356,498	12/1967	Moe et al.	96/1
3,485,738	12/1969	Carreira	96/1 X
2,383,469	8/1945	Colbert et al.	134/7 X

OTHER PUBLICATIONS

IBM Tech. Discl., Vol. 12, No. 8, Jan. 1970, " Reduction of Toner–Filming in Electrophotographic Printing Processes," Crooks, p. 1229

Nuclear Science Abstracts, Vol. 18, No. 6, Mar. 31, 1964, p. 1153, " The Detex Technique of Decontamination," Catherall et al.

Primary Examiner—George F. Lesmes

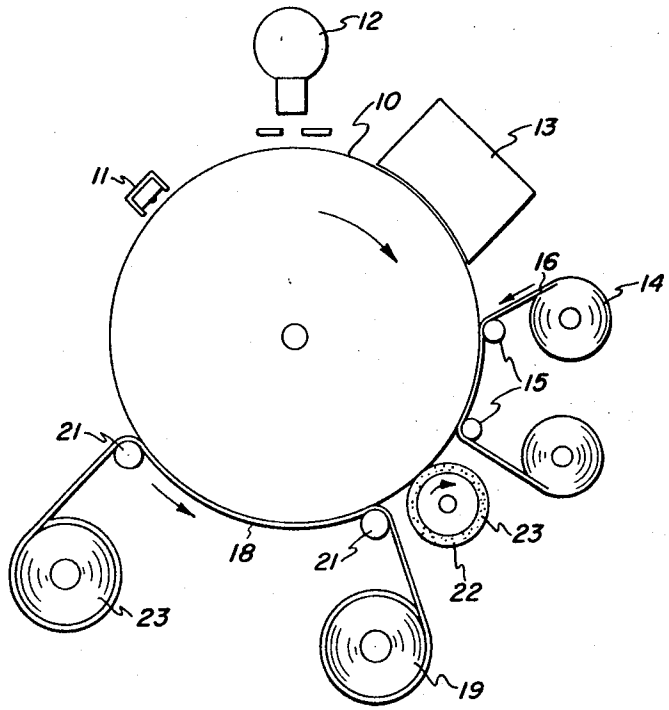
Assistant Examiner—R. E. Martin

Attorney—James J. Ralabate, Albert A. Mahassel and Samuel E. Mott

[57] **ABSTRACT**

A liquid development imaging system with a cycling imaging surface to which is cyclically applied a film forming insulating solid that wets the imaging surface and sharply liquefies with low melt viscosity at a temperature above ambient operation temperature. The added solid permits relative ease in cleaning and the ability to cycle the imaging surface without complete cleaning.

24 Claims, 1 Drawing Figure



INVENTORS
ALAN B. AMIDON
JOSEPH MAMMINO

BY

Samuel E Mott
ATTORNEY

CYCLIC IMAGING SYSTEM

BACKGROUND OF THE INVENTION

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

The formation and development of images on the surface of photoconductive materials by electrostatic means is well known. The basic electrostatographic process, as taught by C. F. Carlson in U. S. Pat. No. 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. No. 2,618,552; the "powder cloud technique" disclosed by C. F. Carlson in U. S. Pat. No. 2,221,776 and the "magnetic brush" process disclosed, for example in U. S. Pat. No. 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 charge 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.

A further technique for developing electrostatic latent images is the liquid development process disclosed by R. W. Gundlach in U. S. Pat. No. 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 field or image areas only. The developer liquid may be pigmented or dyed. The development system disclosed in U. S. Pat. No. 3,084,043 differs from electrophorectic 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 nonimage 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 electrophorectic developers functions only as a carrier medium for developer particles.

In copending application of Alan B. Amidon, Joseph Mammino and Robert M. Ferguson, Ser. No. 839,801, filed July 1, 1969, and entitled Imaging Systems, a technique is disclosed wherein an electrostatic latent image is developed by placing the imaging surface adjacent a patterned applicator surface having a substantially uniform distribution of raised portions of "lands" and depressed portions or "valleys" and containing a relatively non-conductive liquid developer in the depressed portions of the applicator. Liquid developers having a conductivity of up to about 10^{-14} (ohm cm.)$^{-1}$ are surprisingly attracted to the image portions without any substantial electrophoretic separation of particles from the liquid.

While capable of producing satisfactory images, these liquid development systems can be improved upon in certain areas. Particular areas of improvement include those liquid development systems employing reusable or cycling imaging surfaces. In these systems, for example, a photoconductor such as a selenium or selenium alloy drum as the photoconductor surface 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 imaging surface in image configuration. Thereafter, the developer pattern on the imaging surface is transferred to copy paper and the liquid developer may be absorbed by the paper to form a permanent print. During the transfer operation, not all the liquid developer is transferred to the copy paper and a considerable quantity remains on the imaging surface. In order to recycle the imaging surface, this residual developer must be either removed or immobilized; otherwise it will tend to be present as a background in subsequent cycles. If the liquid developer is relatively conductive having a resistivity less than 10^{10} ohm centimeters, any residue remaining on the imaging surface may damage charge acceptance of the imaging surface by laterally dissipating electrostatic charge subsequently put on it. Furthermore, lateral conductivity of residues of conductive liquid developer on the imaging surface may become excessive and the resolution of the resulting image will be poor. On repeated cycling, there is also a progressive accumulation of liquid developer on the imaging surface since in each cycle not all the developer is transferred to the copy paper. This progressive accumulation of developer residue results in an overall loss of density, deterioration of fine detail and contributes to increased background deposits on the final copy particularly since accurate imaging on the imaging surface may be inhibited.

Procedures to remove the developer liquid from the surface of a photoconductor have been employed. However, to provide the necessary removal of ink film, the cleaning step must be so severe and complete that there may be a progressive degradation of the imaging surface lessening its useful life span. The severity of the cleaning step is dictated by the fact that in cleaning a liquid film from a surface, the film is progressively split so that on each separate cleaning, about one half the liquid remains on the photoconductive surface. The cleaning solvents generally necessary to provide adequate cleaning frequently are major contributors to the chemical attack of the imaging surface and are frequently hazardous due to their volatility and toxicity. In some instances and with complete removal of the ink film, the electrical properties of a photoconductor for example, are virtually destroyed by the

cleaning operation after only a small number of cycles. In other instances, the cleaning solvents employed may act as solvents for the resin binder in a binder plate or may induce crystallization of the thin layer of selenium.

SUMMARY OF THE INVENTION

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

It is another object of this invention to provide a novel cleaning system.

It is another object of this invention to provide a thorough and fast cleaning technique.

It is another object of this invention to provide a cleaning system which does not degrade imaging surfaces.

It is another object of this invention to provide a simple cleaning system capable of cyclical use.

It is another object of this invention to provide a dry method of cleaning reusable imaging surfaces.

It is another object of this invention to provide a liquid development system wherein an electrostatographic imaging surface may be repeatedly recycled without appreciable degradation of electrical properties.

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

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 imaging system employing a reusable or cycling electrostatographic imaging surface and having a cleaning system which enables cyclic cleaning of residual liquid developer without imaging surface degradation and without desired buildup of residual developer on the imaging surface. More specifically, in a liquid development system employing a cycling or reusable imaging surface the imaging surface with any residual developer remaining on it is cyclically treated with a film forming insulating solid which sharply liquifies at a temperature slightly elevated over ambient temperature, wets the imaging surface and solidifies to form a film on the imaging surface which improves the removal of residual developer.

The coined generic term "cleanfilm" is intended to be descriptive of the large group of materials which possess to a varying but sufficient degree the stated properties.

The cleanfilm materials employed in this invention have critical surface tension values generally equal to or less than the critical surface tension of the imaging surfaces. Generally, the critical surface tension defines the wettability of a solid surface by noting the lowest surface tension a liquid can have and still exhibit a contact angle greater than zero degrees on that solid. The critical surface tension value for a given solid is determined by observing the spreading behavior and the contact angle of a series of liquids of decreasing surface tension. A rectilinear relationship exists between the cosine of the contact angle and the surface tension of the liquid. The intercept of this line with a line where the cosine of the contact angle equals 1 provides a value of the critical surface tension which is independent of the type of test liquid and is a parameter characteristic of the solid surface only. For further details as to the determination of the critical surface tension of a solid surface, reference is made to the discussion in the Journal of Colloid Science, Vol. 7, 1952 beginning at page 109. The critical surface tension values employed herein and in the claims are based on measurements made between about 20°and about 25° C.

Typically the critical surface tension for the cleanfilms employed in this invention is from about 15 dynes/cm to about 40 dynes/cm provided it is not more than about 10 dynes/cm greater than the critical surface tension of the imaging surface. Images of best quality are obtained when the critical surface tension is from about 20 dynes/cm to about 35 dynes/cm and is at least about 5 dynes/cm less than the critical surface tension of the imaging surface.

The cleanfilms are electrically insulating having a resistivity greater than about 10^{10} ohm cm. Increased charge retention and image preservation in electrostatographic imaging systems are obtained with preferred resistivities exceeding about 10^{12} ohm-cm when the cleanfilms are in the solid state.

The cleanfilms generally exhibit low melting points and preferably have sharp melting points to provide the desired simple rapid liquification on each cycle. Typically, in a commercial machine concept the cleanfilms will have melting points above normal ambient machine operation temperatures. The cleanfilms may be brought to the melting point by the application of external heat or by the application of frictional heat. Typical melting temperatures are from about 25° to about 95° C. When the imaging surface is an amorphous selenium photoreceptor, it is preferred to provide a cleanfilm having a melting temperature of from about 28° to about 65° C. since at temperatures above about 65° C. the amorphous selenium tends to crystallize to the trigonal state which is relatively conductive and therefore less suitable for cyclical use. Imaging surfaces which do not soften or crystallize and can be operated at higher temperatures can be employed with cleanfilms of correspondingly higher melting temperatures provided suitable means are provided for heating them to their melting point. The solid film formers in general are preferably compatible with the liquid developer to provide optimum cycling ability. In other words, the film formers are preferably partially miscible with the liquid developers. Since imaging may take place through a thin film of the cleanfilm distributed or spread on the imaging surface, the film formers are preferably substantially transparent and not opaque or translucent in film thickness of the order of 5 microns or less. Since the film formers are applied as solids and liquified to form the liquid film and may subsequently solidify as a solid film, the cleanfilms are preferably not too brittle or easily fracturable at ambient conditions of use. In addition, the solid materials should add lubricity to the residual developer and preferably do not become tacky when liquified. For rapid distribution of the cleanfilm over the imaging surface when it is liquified, the cleanfilms preferably have a low viscosity at the melting point and a sharp melting point. Typically, the viscosity at the melting point is from about 1 to about 1,000 centipoises. Particularly satisfactory cycling ability is obtained with viscosities of from about 1 to about 100 centipoises.

In addition to the above properties, the cleanfilms of this invention are preferably relatively nonodorous, nonvolatile, and nontoxic to provide optimum safety and comfort to the user.

Any suitable material possessing these properties to varying but sufficient degrees may be employed. Since the solid cleanfilms preferably have sharp melting points to thereby provide quick simple liquification during each cycle the microcrystalline waxes are particularly effective materials. Typically the materials are selected from the group of materials referred to as wax-like solids and liquids found in nature and to the individual constituents of these naturally occurring wax-like materials irrespective of their source or method of preparation. Typical materials included in this group are hydrocarbons, long chain fatty acids, alcohols, ketones and esters. Synthetic compounds which are not waxes from the standpoint of chemical composition but which do have waxy physical characteristics may also be used. Typical materials of this latter group include silicon waxes, polyethylene waxes, fluorocarbon waxes, fatty acid amides, high molecular weight phthalamides, polymers of alkylene oxides and terphenyls.

Typical silicone derivatives include fatty acid esters of polysiloxanes. Particularly satisfactory cycling ability is obtained with the stearyl esters of dimethyl polysiloxane such as poly (dimethylsiloxy) stearoxysiloxane, poly (diethylsiloxy) stearoxysiloxane, poly (dipropylsiloxy) stearoxysiloxane, poly (methyl ethylsiloxy) stearoxysiloxane, poly (dimethylsiloxy) palmitoxysiloxane, poly (dimethylsiloxy) behenoxysiloxane, poly (dimethylsilozy) myristoleoxysiloxane, poly (dimethylsiloxy) 2-hydroxystearoxysiloxane, and poly (dimethylsiloxy) 12-hydroxystearoxysiloxane.

Typical fluorocarbon waxes include the low melting fluorocarbon materials available from E. I. du Pont de Nemours and identified as Freons. Tetrachloridifluoroethane is particularly effective in providing enchanced cycling ability. Other typical fluorocarbon materials include Vydax AR, a dispersion of a waxy tetrafluoroethylene telomer in Freon TF, Krytox fluorinated solids formed by polymerizing hexafluoropropylene epoxide, all available from E. I. du Pont de Nemours; and Kel F waxes which are polymer of chlorotrifluoroethylene, available from Minnesota Mining and Manufacturing Company. Additional typical materials include hexadecafluoro-1-nonane, eicosafluoro-1-undecane, hexadecafluoro-1-nonal, eicosafluoro-1-undecanol.

Typical hydrocarbon waxes may generally comprise saturated hydrocarbons of carbon chain from about 18 to about 70 carbon atoms. Typical materials comprise eicosane, hexeicosane, docosane, tricosane, tetracosane, pentacosane, 13-methyl pentacosane, 2-methyl pentacosane, hexacosane, heptacosane, octacosane, isoactacosane, nonacosane, triacontane, dotriacontane, tritriacontane, pentatriacontane, hexatriacontane, tetracontane, dotetracontane, tetratetracontane, pentacontane, tetrapentacontane, hexacontane, dohexacontane, tetrahexacontane, hexahexacontane, heptahexacontane, heptacontane, cerane, melissane. Particularly satisfactory cycling ability is obtained with hydrocarbon waxes of from about 18 to about 35 carbon atoms such as octodecane, eicosane, tetracosane, pentatriacontane, and mixtures thereof. Eicosane is especially preferred in obtaining optimum cycling ability and may generally be employed as the sole constituent of the additive or be present in major proportion in a mixture of hydrocarbon waxes.

Typical unsaturated hydrocarbon waxes include octadecylene, eicosylene, 1-heneicosene, docosylene, 1-tricosene, tetracosylene, 1-pentacosene, hexacosylene, ceratene, octacosylene, 1-nonacosene, melene, 1-hentriacontene, 1-dotriacontene. Preferred materials providing long lasting cycling ability are eicosyline and 1-heneicosene.

Typical long chain aliphatic alcohols that may be employed include lauryl alcohol, tridecyl alcohol, myristyl alcohol, pentadecyl alcohol, cetyl alcohol, margaryl alcohol, stearyl alcohol, nonadecyl alcohol, arachidyl alcohol, heneicosyl alcohol, benhenyl alcohol, tricosyl alcohol, lignoceryl alcohol, n-lignoceryl alcohol, aryl alcohol, 1-octacosanol pentacosyl alcohol, and hexacosyl alcohol. Preferred materials providing enhanced cycling ability are myristyl alcohol and tridecyl alcohol.

Typical esters that may be employed include the alkyl esters of long chain fatty acids such as palmitic and stearic acid. Typical alkyl esters include the methyl, ethyl, propyl, butyl, amyl, isoaryl, octyl, decyl and cetyl esters. Also included are cetyl laurate, lauryl myristate, myristyl myristate, cetyl myristate, cetyl palmitate, octadecyl palmitate, cetyl palmitate, myricyl palmitate, lauryl stearate, cetyl stearate, stearyl stearate, cetyl stearate, myricyl stearate, myricyl isobehanate, myricyl cerotate, ceryl myricinate. Preferred cycling ability is obtained with lauryl myristate and myristyl myristate.

Typical ketones that may be employed include among others those produced from the catalytic treatment of the higher fatty acids such as palmitone and stearone and those prepared by the Friedel-Crafts condensation of fatty acids with cyclic hydrocarbons such as furyl heptadecyl ketone, methyl furyl heptadeayl ketone, dibenzo furyl hexadecyl ketone and phenoxy-phenyl heptadecyl ketone. Superior cleaning and cycling ability are obtained with furyl heptadecyl ketone and stearone.

Typical fatty acids include both saturated and unsaturated materials such as capric, lauric myristic, 4-hydroxy myristic, palmitic, margaric, stearic, 4-hydroxy stearic, nonadecyclic, 11 hydroxytriadecanic arachidic, madullic, behenic, tricosanic, lignoceric, hexanconsanic, octacosanic, triacontanic, lacceric, 9-eicosenoic, isoerucic, trans-5-tetracosenoic. The fatty acids may also be employed in the form of a suitable metal salt. Superior cleaning and cycling ability is obtained with capric and lauric acids.

The cleanfilms of this invention may be applied to the surface to be cleaned in any suitable manner. Typically, they may be dusted, sprinkled, brushed, cascaded across the surface and applied as a powder cloud. The film formers may also be applied by wiping with cleanfilm impregnated or coated sheets, webs, papers, rolls and cotton wadding. They may also be applied as an aerosol spray. In providing uniform cleaning and to minimize problems of dust, it is preferred to apply the cleanfilms in the form of coated or impregnated webs, sheets or rolls. After the cleanfilms are applied they are liquified by the application of heat in any suitable manner from any suitable source. The necessary heat may, for example, be supplied from an external source or it may be supplied by means of friction. A particularly effective means for applying the cleanfilms is to liquify or dissolve the cleanfilm and then impregnate a roller applicator such as a porous polyurethane roller and heat, if necessary, to drive off any solvent. The polyurethane applicator roll may also be supplied with cleanfilms by rotating in contact with one portion of a solid block of the cleanfilms. The cleanfilm impregnated roller is placed in contact with the imaging surface and applies the film former to the imaging surface. Sufficient pressure or frictional resistance may be applied between the impregnated roll and the imaging surface to create sufficient heat to liquify the cleanfilm and distribute the liquid over the imaging surface. To provide rapid distribution of liquified cleanfilm to the imaging surface and to insure rapid liquification, it is preferred to operate the applicator roll counter to the direction of the imaging surface and to clean the imaging surface after treatment with the cleanfilms described herein with a counter-direction moving absorbent web.

The invention may be further illustrated by reference to the figure of the accompanying drawing in which the figure is a schematic view of an embodiment of an electrostatographic imaging system of this invention. The figure depicts an electrostatographic imaging surface here illustrated as a rotatably mounted cylindrical drum photoconductor **10** such as a selenium drum. The drum is charged at charging station **11** and exposed to a light-and-shadow image at exposure station **12**. The electrostatic latent image is developed at development station **13** and the developer on the photoconductor is transferred in image configuration to a receiving surface **16**, such as ordinary paper which may be moved through the transfer zone in contact with the drum at the same speed and in the same direction as the periphery of the drum. The paper to which the developed image is transferred is supplied from supply roll **14** and is held in transfer position by idlers **15**. The cleanfilm of this invention is applied to the imaging surface by porous roll **22** rotating in contact with photoconductor drum. The porous roll **22** has pores **23** impregnated with solid cleanfilm and cyclically supplied sufficient material to the imaging surface to enable cyclic imaging. The cleaning web **18** is slowly advanced from supply roll **23** through idlers **21** into wiping contact with the imaging surface and finally onto takeup roll **19**.

The cleanfilms are generally applied to the imaging surface in an amount effective to facilitate repeated cycling of the imaging surface without substantial loss of image quality. Generally, from about 0.5 to about 15 milligrams of cleanfilm per hundred square centimeters of imaging surface is effective. Particularly satisfactory cleaning results are obtained with a preferred range of from about 2 to about 12 milligrams per hundred square centimeters. Best cleaning results are obtained within an optimum range of from about 2 to about 8 milligrams per hundred square centimeters of imaging surface.

The theory behind which the cleanfilms of this invention function is not fully understood. It is observed however, that the cyclic addition of the cleanfilms of this invention renders the imaging surfaces dramatically easier to clean. It is currently believed that the cleanfilms may have a greater affinity for the imaging surface than the liquid developer and preferentially form a thin film between the imaging surface and the liquid developer which permits the developer liquid to be removed more readily from the imaging surface. It is also speculated that the cleanfilms may function to decrease the

viscosity of the liquid developer and thus make it easier to remove the liquid developer during cleaning.

While the cleaning technique is not a complete cleaning of the imaging surface the layer of cleanfilm and liquid developer that forms on the imaging surface reach a steady state condition after which there is no further build-up. This static condition generally results in the formation of a very thin layer of cleanfilm on the imaging surface which may well act as a solid lubricating layer thereby facilitating the removal of the liquid developer. This substantially smooth, continuous thin film of residual developer intermixed with cleanfilm achieved during steady state conditions is generally less than about 0.4 microns thick and preferably is less than about 0.25 microns thick. Generally the cleanfilm is applied in solid form and liquified on the imaging surface. It may, however, be applied as a liquid. To achieve accurate cyclic imaging, it is preferred that the cleanfilm intermixed with liquid developer not form a deformation image during any exposure step. To this end, it is preferred that the clean film be present as a nondeformable mixture prior to subsequent exposure step.

Since the cleaning technique of this invention is not a complete cleaning of the imaging surface but rather provides a thin film on the imaging surface which film may comprise any of the selected cleanfilms and residual liquid developer, the developers employed preferably are relatively nonconductive to permit cyclic charging and imaging where necessary without the dissipation of charge by a conductive film. Any suitable liquid developer having these properties may be used. Typically, the developers for which the cleanfilms of this invention are effective have conductivities of from about 10^{-10} (ohm cm.)$^{-1}$ to about 10^{-14} (ohm-cm.)$^{-1}$. Typical materials within this group include mineral oil, the vegetable oils including castor oil, peanut oil, coconut oil, sunflower seed oil, corn oil, rapeseed oil and sesame oil. Also included are mineral spirits; fluorocarbon oils such as Du Pont Freon solvents and Krytox oils; silicon oils, fatty acid esters and oleic acid. In addition, as is well known in the art, the developer may contain one or more secondary vehicles, dispersants, pigments or dyes, viscosity controlling additives or additives which contribute to fixing the pigment on the copy paper.

Any suitable imaging surface may be cleaned with the technique of this invention. Basically, any surface upon which charge pattern may be cyclically formed or developed may be employed. Typical electrostatographic imaging surfaces include dielectrics such as plastic coated papers, xeroprinting masters and photoconductors and photoconductors overcoated with suitable dielectrics. 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-trinitrofluoroenone. 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. For most effective cleaning, it is preferred to provide a surface to be cleaned which has a very smooth surface since generally the smoother and more uniform the surface, the better will be the cleaning.

When a recycling or reusable photoconductor is employed as the electrostatographic imaging surface in the development systems according to this invention, it may be desirable to add a small amount of an appropriate Lewis acid or base to the cleanfilm. Unless an appropriate Lewis acid or base has been provided as a constituent of the liquid developer according to the technique described by J. Mammino and A. Amidon in application Ser. No. 838,328 entitled Imaging Systems and filed July 1, 1969, it is preferred to provide a small amount of this additive in the cleanfilm. The addition of an appropriate Lewis acid or base enables the photoconductors to maintain their ability to accept and hold charge for every imaging cycle. The mechanism by which this is accomplished, however, is not fully understood at the current time. However, by providing a small amount of an appropriate Lewis acid and Lewis base, the electrical properties of reusable photoconductors may be cyclically rejuvenated and imaging quality through successive imaging steps maintained. For any particular photoconductor, the additive to the cleanfilm is specially selected between the two groups of materials, Lewis acids and Lewis bases. Generally, for photoconductors which are positively charged, Lewis bases are employed and for photoconductors which are negatively charged, Lewis acids are employed. Typical examples of Lewis bases include among others, the triarylmethane dyes such as crystal violet, malachite green, pararosaniline, basic fuchsin; xanthane dyes such as rhodamine B, eosin, erythrosine and fluorescein; aniline dyes such as nigrosine and aniline black, solid soluble porphyrin derivatives such as tetraphenyl porphine and copper chlorophyllin; thionine dyes, such as methylene blue and thionine; amines such as triphenyl-amine, polycyclic aromatic and heterocyclic compounds such as anthracene, pyrene, fluorene, acridene, carbazole and their basic derivatives, aromatic hydroquinones, diamino phenyl oxazoles and triazin. Typical Lewis acids include among others, indanthrone dyes, such as anthrazole blue IBC, azo dyes such as naphthol blue black B, benzoazurin G; aromatic compounds such as 2,4,7-trinitrofluorenone, tetrachorophthalic anhydride, chloranil, fluoranil, anthraquinone, and 2-dicyanomethylene-1,3-indanedione. The Lewis base nigrosine is a particularly preferred material in obtaining optimum rejuvenation of electrical properties for positively charged selenium or selenium alloy photoconductor.

The appropriate Lewis acid or base should be present at least in an amount necessary to maintain the electrical properties of a cycling photoconductor. For better cycling characteristics it is preferred that they be uniformly dispersed throughout the cleanfilm in order to insure complete availability to the entire photoconductor surface and to insure maximum rejuvenation and stabilization of the photoconductor. An appropriate Lewis acid or base may be employed in any suitable amount. To provide maximum stabilization of the photoconductor, the Lewis acid or base preferably is present in an amount of from about 0.1 to about 1 percent by weight of the cleanfilm.

After the application of the cleanfilm of this invention, the imaging surface is cleaned of residual material Any suitable cleaning technique or material may be employed. Typical techniques, include the use of wiper blades, such as a polyurethane wiper blade, squeegee rolls, absorbent webs of paper or cloth and brushes. Particularly satisfactory cleaning results are obtained with a web cleaner moving counter to the direction of the advancing imaging surface. Such a web provides satisfactory cleaning by absorbing residual material when advanced at a rate of about 1 inch per 400 inches of imaging surface. The cleaning web may be in contact with the imaging surface from light or touch contact up to a pressure of about 5 pounds per lineal inch. Best cleaning results are obtained with contact pressures of from about 0.5 to about 2 pounds per lineal inch. A particularly preferred web cleaner comprises a nonwoven fabric consisting of about 45 percent cotton fibers wound with a polyamide type resin binder.

DESCRIPTION OF PREFERRED EMBODIMENTS

The following preferred examples further define, describe and compare preferred materials, methods and techniques of the present invention. Examples I, II, III and IV are presented for comparative purposes. In the examples, all parts and percentages are by weight unless otherwise specified.

EXAMPLE I

A clean 8-inch-diameter selenium drum comprising a surface layer of selenium about 50 microns thick on a conductive aluminum substrate is positively charged and exposed to a light-and-shadow image in conventional manner. The electrostatic latent image thus formed is developed by moving a patterned surface applicator roll having developing quantities of developer in the depressed portions thereof past the image bearing surface so that liquid developer is pulled out of the

depressed portions to the image bearing surface in image configuration. The speed of development is about 10 inches per second. The developer employed is of the following composition:

Drakeol 9	45 parts by weight
Microlith CT	27 parts by weight
Methyl violet tannate VM550	4 parts by weight
Ganex V216	22 parts by weight
Nigrosine SSJJ	0.7 parts by weight

Drakeol 9 is a mineral oil manufactured by Pennsylavania Refining Company having a kinematic viscosity of about 15.7 – 18.1 centistokes at 25° C. and a specific gravity of about 0.85. Microlith CT is a resinated predispersed carbon black pigment composed of about 40 percent carbon black pigment and 60 percent ester gum resin, manufactured by CIBA. Nigrosine SSJJ is a spirit soluble dye available from American Cyanamid. Ganex V216 is an alkylated polyvinyl pyrrolidone compound manufactured by GAF Corporation which serves as additional pigment dispersant and may also be regarded as a secondary vehicle. VM550 is methyl violet tannate flushed pigment in mineral oil available from Magruder Color Company.

The developer on the selenium drum is transferred to bond paper in image configuration. The first print is free of background and has a resolution of about seven line pairs per millimeter. The drum is repeatedly subjected to the charge, expose, develop and transfer cycle. The images obtained on subsequent cycles contain high background due to residual developer on the drum from the preceding cycle. Within three imaging cycles, the image resolution is observed to be less than two line pairs per millimeter.

EXAMPLE II

The procedure of Example I is repeated except that after each image is transferred the selenium drum is wiped with a cotton cloth. Background deposits are observed to increase after each cycle. The fifth print has heavy background and image resolution below two line pairs per millimeter.

EXAMPLE III

The procedure of Example I is repeated except that after the transfer of each developed print, the selenium drum is cleaned with an untreated porous polyurethane sponge roll by rotating the sponge roll in contact with the drum in opposite direction under light contact. After each cycle, the background is observed to increase. The fifth print obtained has heavy background.

EXAMPLE IV

The procedure of Example III is repeated except that the polyurethane sponge roll is impregnated with mineral oil. Following contact with the sponge roll, the drum is wiped with a clean cotton cloth. Results similar to those in Example III are obtained.

EXAMPLE V

The procedure of Example I is repeated except that after transfer of each developed print, the selenium drum is contacted with a polyurethane sponge roll impregnated with eicosane, to deposit 4 milligrams of eicosane per 100 square centimeters of drum surface. Following contact with the sponge roll, the drum is contacted with an absorbent web of Masslinn Nonwoven Fabric S–1000, a rayon fabric available from Chicopee Mills, Incorporated. The web is in contact with about 4 inches of the selenium drum surface under a pressure of about 0.5 inches per lineal inch and is moved counter current to the selenium drum at a rate of about 1 inch of web for every 400 inches of drum surface. The first print has a resolution of five to seven line pairs per millimeter and is free of background. No change in resolution or background is observed after 500 cycles.

EXAMPLE VI

The procedure of Example V is repeated except that the polyurethane sponge roll is impregnated with a mixture of dotriacontane and eicosane in a weight ration of 1 to 10 which is deposited on the imaging surface at a rate of about 8 milligrams per 100 square centimeters. Results similar to those stated in Example V are obtained.

EXAMPLE VII

A xeroprinting master 9 × 14 inches is prepared by placing a thin insulating coating of epoxy resin about 0.0005 inches thick in image configuration on a conductive plate of aluminum. The plate is charged to +450 volts by passing it under a corona charging unit. The image is developed in the manner described in Example I. The cleaning procedure of Example V is repeated except that the polyurethane sponge roll is impregnated with Freon BF, a tetrachlorodifluoroethane available from E. I. du Pont de Nemours and Company, which is deposited at a rate of about 7 milligrams per 100 square centimeters. The first print has a resolution of about 5 to seven line pairs per millimeter and is free of background. No change in resolution or background is observed after 1,000 cycles.

EXAMPLE VIII

The procedure of Example VII is repeated except that the polyrethane sponge roller is impregnated with Dow Corning F–157 Wax, a poly (dimethylsiloxy) stearoxy-siloxane available from Dow Corning, which is deposited at a rate of about 3 milligrams per 100 square centimeters. Results similar to those stated in Example V are obtained.

EXAMPLE IX

The procedure of Example VII is repeated except that the polyurethane sponge roller is impregnated with beeswax which is deposited on the drum surface at a rate of about 2 milligrams per 100 square centimeters. The first print has a resolution of about five line pairs per millimeter and is free of background. Prints of similar quality are obtained for an additional 200 cycles. The beeswax, however, does not melt sharply and is tacky at ambient temperature and tends to smudge thus decreasing the resolution.

EXAMPLE X

The procedure of Example V is repeated except that the polyurethane sponge roller is impregnated with lauric acid which is deposited on the drum surface at a rate of about 4 milligrams per 100 square centimeters. Results comparable to those in Example V are observed.

EXAMPLE XI

The procedure of Example V is repeated except that the polyurethane sponge roller is impregnated with tridecyl alcohol which is deposited on the drum surface at a rate of about 3 milligrams per 100 square centimeters. Print quality comparable to that obtained in Example V is observed for 300 prints.

EXAMPLE XII

The procedure of Example V is repeated except that the polyurethane sponge roller is impregnated with lauryl myristate ester which is deposited on the drum surface at a rate of about 4 milligrams per 100 square centimeters. Print quality comparable to that obtained in Example V is observed for 100 prints.

EXAMPLE XIII

The procedure of Example V is repeated except that the polyurethane sponge roller is impregnated with furyl heptadecyl ketone which is deposited on the drum surface at a rate of about 2 milligrams per 100 square centimeters. Print quality comparable to that obtained in Example V is observed for 350 prints.

EXAMPLE XIV

A clean selenium drum 8 inches 8 diameter comprising a surface layer of selenium about 50 microns thick on a conductive aluminum substrate is positively charged and exposed to a light-and-shadow image in conventional manner. Development of the electrostatic latent image is obtained by rotating the drum such that the surface portion contacts by immersion 9 developer of the following composition by weight:

Mineral Spirits	95 parts by weight
Drakeol 9	2 parts by weight
Microlith CT Black	2 parts by weight
Ganex V216	1 parts by weight

The developer on the selenium drum is transferred to bond paper in image configuration. The first print is free of background and has a resolution of about 30 line pairs per millimeter. The drum is thereafter rotated in contact with a stationary solid stick of Freon BF containing uniformly dispersed therein about 0.5 percent by weight of the Freon BF of Nigrosine SSJJ, to deposit about 10 milligrams of Freon BF per 100 square centimeters of drum surface. Following contact with the stick of Freon BF, the drum is wiped with Masslinn rayon fabric S–1000. This procedure is repeated for an additional 500 prints with no noticeable change in resolution or background.

EXAMPLE XV

The procedure of Example XIV is repeated except that instead of the drum rotating in contact with a solid stick of Freon BF, 5 milligrams per 100 square centimeters of drum surface of a mixture of equal parts by weight of stearyl stearate and Dow Corning F–157 wax containing 0.4 percent Nigrosine SSJJ by weight of the mixtures are sprayed from an atomizer onto the selenium drum. The drum is then rotated in contact with a cleaning web of Masslinn rayon fabric S–1000 in the manner generally depicted in the figure of the drawing under a pressure of about 0.5 pounds per lineal inch. The cleaning web is advanced in contact with about 4 inches of the drum surface and countercurrent to the direction of the rotating drum at a rate of about 400 inches of drum surface to 1 inch of cleaning web. The first print has a resolution of about 40 line pairs per millimeter and is free of background. After repeated cycling of 200 cycles no change in print quality is observed.

EXAMPLE XVI

The procedure of Example XIV is repeated except that the solid stick of Freon BF is replaced by a polyurethane sponge roll impregnated with eicosane containing about 0.5 percent Nigrosine SSJJ by weight of the mixture. The polyurethane roll is rotated in contact with the photoconductor so that the mixture of eicosane and Nigrosine is deposited on the drum surface at a rate of about 4 milligrams per 100 square centimeters. The first print obtained has a resolution of about 30 line pairs per millimeter and is free of background. Prints of similar quality are obtained for an additional 400 prints.

EXAMPLE XVII

The procedure of Example XVI is repeated except that the polyurethane roll is impregnated with a mixture containing about equal parts by weight of octadecane, tetracosane, docosane, and about 0.6 percent by weight of the mixture Nigrosine SSJJ. The mixture is deposited on the photoconductor at a rate of about 3 milligrams per 100 square centimeters. The first print obtained has a resolution of about 35 line pairs per millimeter and is free of background. Prints of similar quality are obtained for an additional 200 cycles.

EXAMPLE XVIII

The procedure of Example XVI is repeated except that the polyurethane roll is impregnated with a mixture containing about equal parts by weight of furyl heptadecyl ketone and stearone and about 4 percent by weight of the mixture of Nigrosine SSJJ. The mixture is deposited on the photoconductor at a rate of about 5 milligrams per 100 square centimeters. The first print obtained has a resolution of about 30 line pairs per millimeter and is free of background. Prints of similar quality are obtained for an additional 250 cycles.

EXAMPLE XIX

The procedure of Example XVI is repeated except that the polyurethane roll is impregnated with a mixture containing about equal parts by weight of 4-hydroxy stearic acid, lauric acid, capric acid and about 0.7 percent by weight of the mixture of Nigrosine SSJJ. The mixture is deposited on the photoconductor at a rate of about 2 milligrams per 100 square centimeters. The first print obtained has a resolution of about 25 line pairs per millimeter and is free of background. Prints of similar quality are obtained for an additional 300 cycles.

The above examples demonstrate the effectiveness in cycling the imaging surface without a complete cleaning on every cycle. Comparison of examples according to this invention show a major startling improvement over the technique of Examples I through IV. It may also be appreciated that the instant invention provides a fast, cheap and efficient cleaning operation and one which provides the advantages of liquid cleaning but does not require the extraordinary handling procedures necessary for both liquids and powders since the cleaning liquid is handled as a dry component. Furthermore, while the technique of this invention does not require the removal of all residual developer and cleanfilm, the removal of quantities of this material which would substantially affect cyclic imaging capability if present on the imaging surface is readily achieved with minimum effort.

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 than those listed above which may be substituted for those in the 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 claim is:

1. The method of cyclically electrostatographically imaging on a reusable imaging surface comprising the steps of: forming an electrostatic latent image on the imaging surface; developing the image with a liquid developer; transferring the developer from the imaging surface to a receiving surface in image configuration; substantially uniformly contacting the imaging surface with an organic film forming solid which sharply liquefies at a temperature slightly elevated over ambient temperature and wets said imaging surface to form a thin film thereon, said film forming solid having a critical surface tension value from about 10–40 dynes/cm and not more than about 10 dynes/cm greater than that of said imaging surface, a resistivity greater than about 10^{10} ohm-cm., a melting point between about 20° C. and about 95° C. and a viscosity at its melting point of from about 1 to about 1,000 centipoises; causing the film forming solid to liquefy and removing excess residual developer and excess film of film forming solid from the imaging surface to prepare the imaging surface for the next cycle.

2. The method of claim 1 including repeating the recited steps of forming, developing, transferring, contacting, causing and removing, at least one additional time.

3. The method of claim 1 wherein the critical surface tension value of said film forming solid is about equal to or less than that of said imaging surface.

4. The method of claim 3 wherein the critical surface tension value of said film forming solid is from about 20–35 dynes/cm and is at least about 5 dynes/cm less than that of said imaging surface.

5. The method of claim 1 wherein said film forming solid has a melting point between about 28° C. and about 65° C.

6. The method of claim 1 wherein said film forming solid has a viscosity at its melting point of from about 1 to about 100 centipoises.

7. The method of claim 1 wherein the excess residual developer and film are removed from the imaging surface by wiping contact with an absorbent material.

8. The method of claim 1 wherein the imaging surface is a reusable photoconductor.

9. The method of claim 8 wherein said film forming solid contains from about 0.1 percent to about 1 percent by weight of said film forming solid of a material selected from the group consisting of Lewis acids and Lewis bases.

10. The method of claim 8 wherein the photoconductor is selected from the group consisting of selenium, selenium alloys and phthalocyanine binder layers.

11. The method of claim 1 wherein said film forming solid is substantially transparent.

12. The method of claim 1 wherein said film forming solid is a hydrocarbon wax.

13. The method of claim 1 wherein said film forming solid is a fluorocarbon wax.

14. The method of claim 1 wherein said film forming solid is a silicone wax.

15. The method of claim 12 wherein said hydrocarbon wax is eicosane.

16. The method of claim 1 wherein said film forming solid has a surface tension which is not more than about 10 dynes/cm.^{2} greater than that of the imaging surface.

17. The method of claim 1 wherein said film forming solid is cyclically added in an amount of from about 0.5 to about 15 milligrams per 100 square centimeters of imaging surface.

18. The method of claim 1 wherein said film forming solid is eicosane which is added in an amount of from about 2 to about 12 milligrams per 100 square centimeters of imaging surface.

19. The method of claim 2 wherein said cleanfilm is a microcrystalline wax.

20. The method of claim 2 wherein said thin film is a substantially smooth surfaced continuous layer less than about 0.4 micron thick.

21. The method of claim 2 wherein said imaging surface is contacted with said film forming solid by moving said imaging surface against a porous material impregnated with said solid.

22. The method of claim 2 wherein said imaging surface is contacted with said film forming solid by moving said imaging surface against a solid stationary supply of said film forming solid with sufficient frictional resistance to liquefy said solid.

23. The method of claim 2 wherein said imaging surface is wiped with an absorbent fibrous web moving against said imaging surface.

24. The method of claim 2 wherein said imaging surface is contacted with said film forming solid by moving said imaging surface against a porous cylindrical roll impregnated with said solid, said roll moving in a direction opposite that of the imaging surface at the line of contact.

* * * * *