

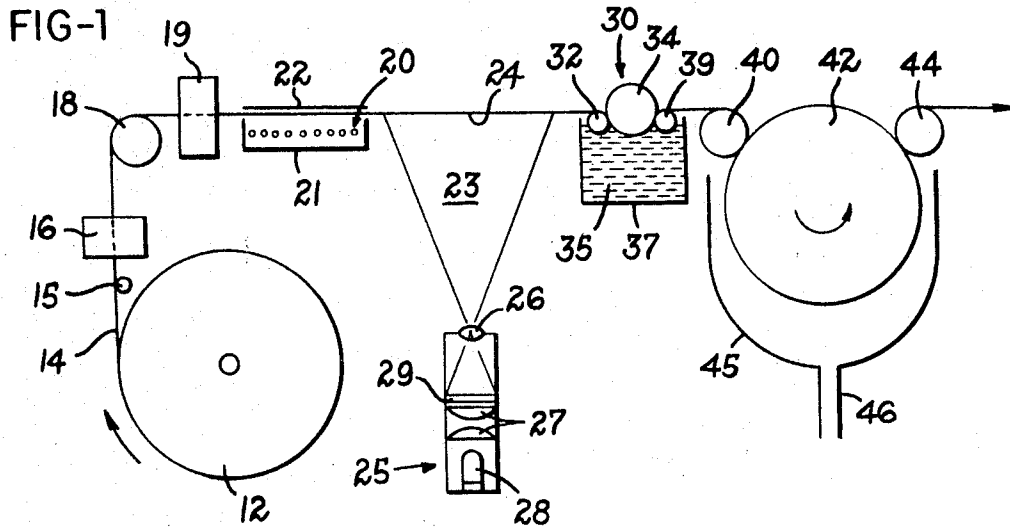
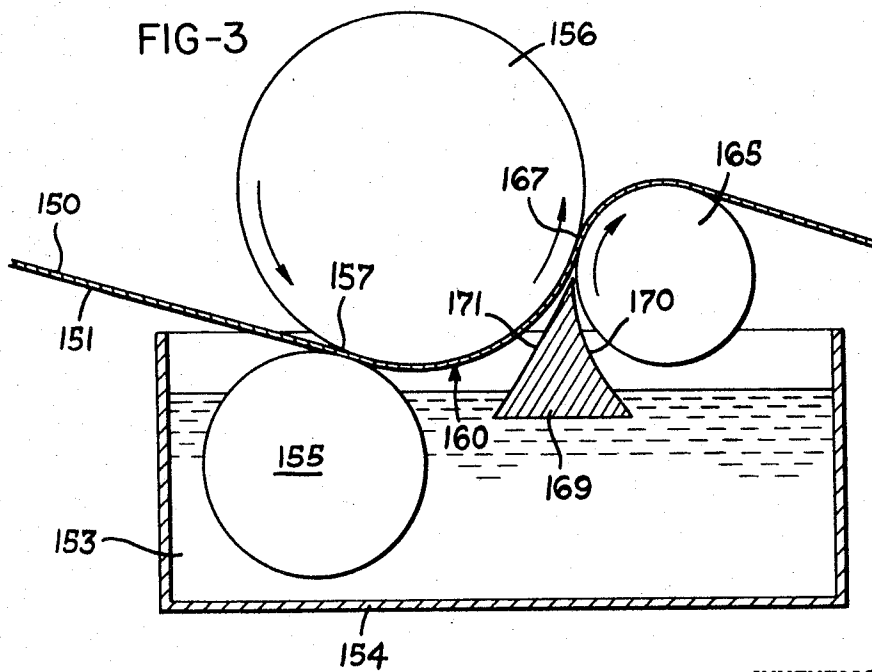
Jan. 31, 1967

D. L. FAUSER ET AL
ELECTROSTATIC PHOTOGRAPHIC PROCESS OF MAKING
MULTI-COLORED PRINTS

3,301,675

Original Filed June 8, 1961

2 Sheets-Sheet 1



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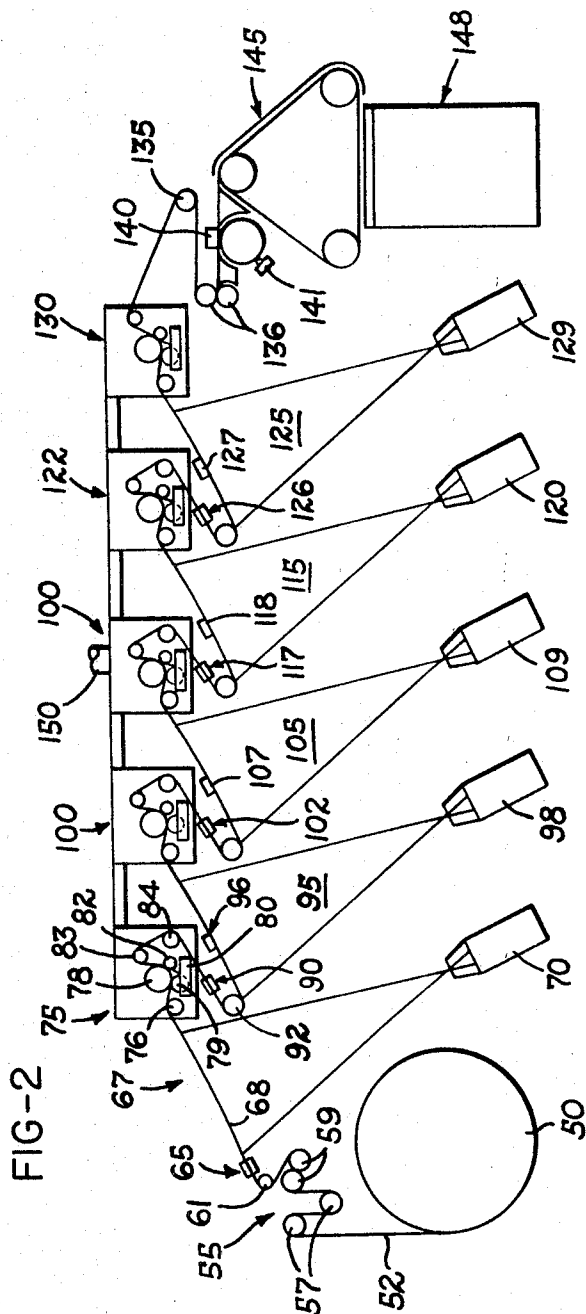


FIG-2

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3,301,675

ELECTROSTATIC PHOTOGRAPHIC PROCESS OF MAKING MULTI-COLORED PRINTS

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Original application June 8, 1961, Ser. No. 115,643, now Patent No. 3,241,957, dated Mar. 22, 1966. Divided and this application Feb. 18, 1965, Ser. No. 433,816
10 Claims. (Cl. 96—1.2)

This application is a division of our application Ser. No. 115,643, filed June 8, 1961, which is a continuation-in-part of application Ser. No. 762,756 filed Sept. 23, 1958.

This invention relates to improvements in electrostatic photography, and more particularly to a combination of imaging materials which are compatible and capable of being utilized to form an image in one color or form a multi-colored image wherein each image remains substantially adhered to an image bearing surface.

In present electrostatic photography systems, a plate is employed having a photoconductive coating thereon, such as selenium adhered directly to a base plate by vapor deposition, which is capable of being uniformly charged and exposed to form an electrostatic latent image. This image may be then developed by use of a powder carrier technique which causes the powder to become attracted to the charged portion of the plate, and thereafter, the developed image is transferred to the paper and fixed thereon, or one may transfer the charge image to the paper and subsequently employ a powder developer to render the image visible, followed by a fixing operation to cause the deposited powder to adhere permanently to the paper. In a system of the above type, the image formed on the paper by either charge transfer or transfer of the powder image may lack the desired quality and definition, and perhaps, the desired quality and definition can be obtained if the image were developed on the surface of the photoconductor and remained thereon.

Another system which has been proposed includes the use of an image receiving member including a finely divided photoconductive material adhered to the surface of a suitable substrate by a film forming binder such as a silicone resin, or a urea or melamine formaldehyde resin, for example. Suitable substrates include paper, plastic films, thin metallic foils, and imaging members of this type are generally referred to as "photoconductive papers," although it is to be understood that the phrase "paper" is not descriptive of the several substrates which are possible.

In contrast to the plate or drum systems heretofore employed, in the "paper" system an electrostatic latent image is formed on the electrophotosensitive surface, and the image is developed thereon without the necessity of transferring the powder image or the charge image, and, the powder image may be fixed directly on the surface of the electrophotosensitive surface in order to impart stability to the image. The use of a photoconductive paper thus eliminates, to a substantial degree, the need for transferring the powder or charge image to paper, however, there may still be the requirement of arranging for the developed image to be fixed in order to provide a permanent image.

Recently, a developer system has been proposed which makes it possible to develop images with improved clarity, contrast and definition. One such system is disclosed in the Metcalfe article "Liquid Developers for Xerography," Journal of Scientific Instruments, volume 32, February 1955, pp. 74 and 75. The developer disclosed in this article represents a simple system including a dispersion of

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finely divided carbon black in an insulating liquid. When such a liquid developer, as above described, is employed under the proper condition with the plates, drums or papers above described, it may be necessary to employ a separate fixing operation in order to achieve the desired stability of the developed image.

It has been noted with hydrocarbon vehicles which are suitable as a dispersing medium for the carbon black that an adverse effect on the resins employed in the photoconductive paper frequently occurs. Brief contact between the paper and the dispersing medium has resulted in a loss of paper stability and brought about dimensional changes due to the swelling action of the medium on the film forming binder. It has been discovered in accordance with the present invention that such dimensional changes may be overcome by a proper correlation of the components of the liquid developer and the resin employed as a film forming binder of the paper in order to provide a compatible system wherein the components of the developer exhibit little, if any, adverse effect upon the image bearing member.

Accordingly, it is a primary object of the present invention to provide electrophotographic systems or arrangements wherein an electrostatic latent image on an image bearing member including a film forming binder is treated with a liquid developer which exhibits little or no adverse effect on the image bearing member, and wherein marking elements of the developer are substantially fixed to the image bearing member as a result of fixing ingredients in the developer in order to provide an image which is substantially permanently adhered to the surface of the image bearing member.

The above object has been accomplished successfully in accordance with the present invention by employing a liquid developer in the form of a dispersion of marking elements in a suitable suspension medium for developing an electrostatic latent image on the surface of an image bearing member. The developer preferably includes a liquid suspension medium or vehicle phase which may be called a liquid carrier, and wherein the liquid medium has an electrical resistivity of approximately 10^9 ohm centimeters or greater. Dispersed throughout the medium is a toner including marking agents or aggregates thereof, which carry in preferential association therewith elements of a macro-molecular binder or the medium may have dispersed therein resin components capable of forming an organosol, in which instance the marking agent may include a resin and a dye material, and charge constituents in sufficient density to develop a zeta potential consonant with the desired electrophoretic mobility through the medium. It is preferred that the elements of the toner include a component capable of effecting a wetting action on the base materials, or the surface bearing the electrostatic latent image, as will be hereinafter described.

The image bearing member employed is preferably of a type including finely divided photoconductive material which is dispersed throughout a film forming binder to form a matrix adhered to a suitable backing member. The film forming resin preferably has a dipole moment which is appreciably different from the dipole moment of the suspension medium, and may be of any of the suitable water soluble resins, for example, polyacrylic and polymethacrylic acid and ester resins, polyacrylic and polymethacrylic amines, and polyvinyl compounds containing functional groups rendering them water soluble, all of which are capable of providing suitable electrical characteristics subsequent to deposition on a suitable substrate. Also suitable as film forming binders in accordance with the present invention are resins which are normally water insoluble but which are capable of being

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rendered temporarily soluble by a transient reaction, as well as resins capable of being deposited by hot melt, organic solvent coating, or emulsion coating techniques.

Illustrative of other suitable film forming binders are polymers and copolymers which may be rendered water soluble under certain conditions, are, for example, partially esterified copolymers, polyvinyl methyl ethermaleic anhydride copolymers which are partially esterified or partially amide, methacrylic acid-vinyl acetate copolymers and others which may be either soluble when neutralized to an alkaline pH but which are not water soluble at an acid pH. The resin-photoconductive matrix deposited on the surface of a suitable substrate, as above described, achieves a water insoluble condition to provide a surface coating which is water insoluble at a neutral pH. Image bearing members of the above type are disclosed in copending applications Ser. No. 640,353, filed Feb. 15, 1957, and Ser. No. 762,699, filed Sept. 23, 1958 now Patent No. 3,155,531, while developers of the above type are disclosed in copending application Ser. No. 762,756, filed Sept. 23, 1958, all assigned to the same assignee as this application.

It is another object of this invention to provide a system of the type previously described for developing electrostatic latent images with a liquid developer of the type described wherein the developer includes a component capable of being polymerized, and wherein the developed image remains substantially permanently adhered to the surface of the image bearing member due to the polymerization of a component of the developer on the surface of the image bearing member.

Another object of this invention is the provision of a system for developing electrostatic latent images wherein a component of the developer reacts or otherwise effects the film forming binder to cause substantial fixing of the marking elements to the surface of the image bearing member.

Still another object of this invention is the provision of electrostatic photography systems employing an image bearing member wherein a relatively finely divided photoconductor dispersed in a film of binder is adhered to a suitable base, and wherein the liquid developer employed includes ingredients exhibiting no adverse effect on the film forming binder.

It is a further object of this invention to provide an electrostatic photography system wherein an electrostatic latent image, formed on a photoconductive matrix including a film forming binder, is treated with a liquid developer including a suspension medium such that the polar nature of the medium is substantially different from that of the film forming binder whereby softening or swelling resulting in dimensional changes of the film forming binder is avoided.

A further object of this invention is the provision of a system for removing sufficient amounts of the suspension medium employed in the liquid developer from the surface of the image bearing member in order to form a relatively permanent image on the surface of the image bearing member, and wherein the removal of the suspension medium is accomplished without materially interfering with the definition and clarity of the deposited image.

Still a further object of the present invention is the provision of a system for forming a composite print by electrostatic photography wherein a plurality of latent images are formed on an image bearing member, and wherein each image is developed by a liquid developer to produce a composite print.

Still another object of the present invention is the provision of a novel system for forming a composite print in multi-colors by electrostatic photography wherein a plurality of latent images are formed on an image bearing member, each representative of a different color, and wherein each image is developed by a liquid developer of a different color to provide a composite print in multi-colors.

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An additional object of this invention is the provision of a system of electrostatic photography for producing a composite image by the successive steps of forming a plurality of latent images and developing each latent image in a desired color, and wherein a high intensity flash source of light is employed to expose an original for a relatively short period of time with a relatively high intensity light source in order to form a usable exposure.

It is still a further object of the present invention to provide a multi-colored electrostatic photography system wherein a registry system is employed to form index marks on an image bearing member, which marks control the subsequent placement or location of further image components of the print so as to enable accurate registration of each image with respect to the others forming a multi-colored print.

Other objects and advantages of the invention will be apparent from the following description, the accompanying drawings and the appended claims.

In the drawing:

FIG. 1 is a diagrammatic view of an electrostatic photography system constructed in accordance with this invention;

FIG. 2 is a diagrammatic view of a multi-colored system constructed in accordance with the invention; and FIG. 3 is an enlarged view of one of the developing systems shown in FIG. 2.

As an aid to simplify or clarify the disclosure hereof, it may be helpful preliminarily to consider generally some factors relating to (1) image bearing members including the film forming resin and photoconductive materials, (2) developer and toner formulations and other considerations, and (3) interaction of the developer and image bearing members.

The term image bearing member as employed in this disclosure and as set forth in the claims is intended to encompass any member which is capable of receiving an image in charge configuration and maintain such a configuration for a period of time sufficient to allow treatment with a suitable developer. It is to be understood that such a member may be a laminated article of the type previously described wherein one surface and possibly two surfaces are capable of receiving an electrostatic latent image either by having one formed thereon directly, or by having one transferred thereto by procedures well known in the art, and may or may not include an electrophotographic surface.

The improved developers employed in accordance with the present invention are primarily three-component systems including a liquid suspension medium, a marking agent and a resin and/or surfactant which is carried in preferential association with the marking agent to form a marking complex or element. The resin and/or surfactant component may be considered a charge control and fixing agent operating to provide a marking complex of the proper charge with respect to the medium and the image in charge configuration present on the surface of the image bearing member.

IMAGE BEARING SURFACES OR MATERIALS

As is well known every molecule is formed of positively charged nuclei and negatively charged electrons, and when a molecule is placed in an electrical field, the action of the field tends to orient the molecule by attracting the positive nuclei toward the negative electrode while the electrons are attracted towards the positive electrode. This orientation is the result of a polarization which takes place such that an electric dipole is formed, which in certain instances lasts as long as the field is applied. Other molecules exhibit an inherent characteristic dipole moment because the centers of positive and negative charge distribution do not coincide, or because the arrangement of the molecule is such that there is a non-equidistant distribution of electron pairs.

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In the case of organic compounds, the presence of certain functional groups such as alcohols, amides, amines, acid radicals, and the like, as well as inorganic groups at one end of the molecule, will impart to the molecule a non-uniform electrical distribution resulting in a dipole moment. In certain instances, the distribution of functional groups acting as electrical centers is symmetrical such that the centers are spaced an equal distance apart from the positive center. Considering a molecule wherein the two electrical centers are spaced apart a distance l , the dipole moment, which is referred to as μ , equals Zl , wherein Z represents the charge magnitude. In instances where the electrical distribution is uniform, the net dipole moment is zero.

To illustrate the above differences in dipole moment as a function of electrical symmetry, those organic compounds which are electrically symmetrical are considered to have a zero dipole moment, such compounds being for example, carbon tetrabromide, carbon tetrachloride, benzene, all linear hydrocarbons and all aromatic hydrocarbons wherein there is no unbalance of electrical distribution. Other materials such as alcohols, amines, amides and organic acids, for example, may have dipole moments ranging from 1.3 to 3.57 as expressed in Debye units. These characteristic dipole moments of the various organic compounds offer a convenient reference point from which the polar or non-polar characteristics of the molecule may be ascertained. As a general rule those compounds exhibiting a high dipole moment are said to be polar, while those exhibiting a very low dipole moment, or a zero net dipole moment, are said to be non-polar.

In considering the film forming resins which may be used in accordance with the present invention, it is preferred that the resin be polar in nature, or formulated to include polar monomer units, that is, having a relatively high dipole moment to provide a film coating which is stable with respect to the components of the developer. The photoconductive material is generally in the form of finely divided organic or inorganic particles dispersed in a binder to form a matrix permanently adhered to a base member. Reactions may take place between the components of the liquid developer and the film forming resin which result in dimensional changes of the matrix or image bearing surface. Such dimensional changes are objectionable since they may cause appreciable distortion in the final print, or produce other undesirable secondary effects.

Dimensional changes may result because a component of the developer is able to cross-link or penetrate within the molecular structure of the film forming binder, such penetration being, perhaps, a result of hydrogen bonding by which a hydrogen atom from a component of the liquid developer becomes interchanged with a hydrogen atom in the film forming binder. If a major source of swelling of the film forming binder be the type of compound employed as the suspension medium for the liquid developer, utilization of a film forming binder which is polar in nature and a suspension medium for the developer which is non-polar in nature, operates to effect substantial reduction of such undesirable swelling.

It is to be understood that such swelling may not necessarily be an instantaneous procedure but may progress over a period of time, and ultimately an equilibrium condition is achieved wherein little, if any, additional swelling results after prolonged contact with the suspension medium. Thus, if equilibrium conditions are established before dimensional changes take place in the film forming resin or binder, the film forming binder may be considered compatible with the suspension medium or any other component in the liquid developer. It is preferred in accordance herewith that the equilibrium condition be achieved at a point such that substantially no swelling or removal of the film forming resin from the base occurs generally within the time for normal processing. Ex-

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pressed in another fashion, the film forming binder should be compatible with the liquid developer to the extent at least that, within the residence time of the image bearing surface in contact with the developer, there is little, if any, dimensional change in the film forming resin.

Even if the degree of swelling is not sufficient to create any appreciable dimensional changes in the image bearing surface, still such swelling may bring about certain ancillary undesirable conditions resulting in background deposits or an increase in tack which ultimately produces a viscous entrapment of the marking elements of the developer in those areas of the image bearing surface which should not have any deposit formed thereon. The tendency for dimensional changes to take place is of considerable significance in relation to multi-color work wherein an image bearing surface is sequentially treated with a plurality of liquid developers as will be described more fully hereinbelow.

As was mentioned above, every organic compound has a characteristic charge distribution. If swelling occurs due to hydrogen bonding or cross-linking, the inherent charge distribution is altered in those areas where the hydrogen bonding has taken place resulting in a decrease in the polar nature of the resin and possibly an alteration in the electrical resistance of the surface of the image bearing member. If it is assumed that the surface of the film forming resin possesses an inherent positive charge, there may be an interference with the distribution of such a charge as a result of the swelling taking place.

The inherent charge distribution, above described, is attributable to the nature of the molecules constituting the film forming binders and gives rise to van der Waal's forces or uniform weak force fields which tend to promote adhesion of any element which is brought within the influence of the force fields, a feature which is desirable especially with respect to those marking elements attracted to the surface by the presence of a field condition attributable to an electrostatic latent image.

As the film forming resin swells or becomes solvated, the viscosity and modulus is reduced as a result of the swelling, and the tack of the coating is increased resulting in undesired viscous entrapment of marking elements.

From the above discussion, it can be seen that even if the action of the suspension medium on the resin does not cause swelling to such a degree as to result in severe distortion or separation of the film forming binder from the substrate, there may very well take place important ancillary or secondary effects which may increase background deposit or disturb the inherent charge relationship between the marking element and the film so that secondary fixation attributable to van der Waal's forces will be disturbed from the desired condition.

One feature of the present invention relates to controlling the softening of the film forming resin or binder such that an equilibrium condition is established before dimensional changes take place in the film forming binder, which softening is advantageously employed to hold the deposited particles and accomplish fixing of the deposited developer for providing a print which exhibits considerable stability to smudging or smearing. In operation, the components of the developer are coordinated or correlated with respect to the film forming binder so as to effect establishing an equilibrium condition at which the film forming resin is softened to a point such that the deposited elements of the developer are capable of being embedded or at least partially embedded in the surface of the image bearing member. Establishing an equilibrium condition before dimensional changes take place, and one in which the film forming binder is softened without causing dimensional changes thereof, operates satisfactorily to provide a fixed image as will be described more fully hereinbelow and especially with reference to the specific examples to follow.

In accordance with the present invention, film forming binders are employed which are polar in nature to

effect substantial physical stability of the resin in the presence of non-polar suspension mediums so that swelling, as well as the adverse secondary effects noted above, are substantially eliminated. It has been found that the resins employed as film forming binders in accordance with copending application Ser. No. 640,353, mentioned above, operate to produce satisfactory results and possess the desired characteristics which have been noted above.

Typical or illustrative examples of resins with which satisfactory results have been obtained in accordance herewith are disclosed in said copending application and it is intended that such examples be incorporated herein by reference.

It is to be understood that the above discussion applies to the characteristics of the film forming resin which are desirable in the absence of any uniform potential applied to the surface of the resin as by corona charging, and the like, since the condition of the surface in a non-charged state will assist in controlling background deposition and definition during the electrophotographic process. The formation of image and non-image or background areas serves to attract the marking elements in a preferential manner from the developer dispersion while the inherent electrical condition of the film forming resin matrix operates to maintain background deposits at a desirable low level, and thus the undesirable ancillary side effects attributable to swelling, etc., as noted above, are substantially eliminated, or minimized.

It is also possible in accordance with the present invention to employ the principles of viscous entrapment, above described, in order to form a positive print from a negative original especially in line work, although such a system is not limited thereto. In operation, an electrostatic image corresponding to the negative may be formed and a developer employed which is repelled by the image areas and deposits in the non-image areas because of controlled viscous entrapment and the other secondary effects previously noted in order to provide a positive print from a negative original. In the usual process of electrostatic photography, it is desired to have the marking element attracted to those portions of the image bearing surface which are charged in order to produce a developed image corresponding to the original. However, in the mode of operation previously described, the charged portions of the image bearing surface operate to repel the marking elements and viscous entrapment is employed to effect deposition of the marking elements in the non-charged areas.

As can be understood from the preceding discussion, the substrate upon which the electrophotographic matrix is deposited is preferably formed of a material which is relatively stable in the presence of components included in the liquid developer, that is to say, the components of the liquid developer and the composition of the substrate are coordinated and correlated such that the substrate does not undergo dimensional changes resulting in destruction or dimensional changes in the image bearing surface itself. This is especially true with respect to multi-color work wherein the image bearing surface is successfully treated with a series of developers as will be described more fully hereinbelow.

In addition, it is preferred that the electrophotographic surface formed on the substrate be continuous in nature in order to prevent the developer from penetrating through the electrophotographic matrix into the body of the paper and possibly causing swelling of the fibers thereof. Such a characteristic of the coating is of interest especially with the squeegee system which will be described in connection with the interaction between the liquid developer and the film forming resin.

TONERS AND DEVELOPERS

As illustrative of the operation and enhanced results achievable by liquid developer systems embodying and for practicing this invention, the following specific ex-

amples are noted among those with which satisfactory results in the development of electrophotographic images according to this invention are obtained:

Example I

A dispersion of black iron oxide pigment in Varnolene (a petroleum derivative indicated as number 3039 and supplied by the Sohio Oil Company) was achieved by intimately admixing iron filings with a quantity of iron oxide pigment or powder (to break up agglomerations in the latter), and then pouring the filing-oxide mixture into Varnolene, as a result of which charged iron oxide particles floated off into a dispersion in which the development was conducted. Fixing was accomplished by overcoating the developed image, after evaporation of the Varnolene vehicle by forced air drying, with a water solution of polyacrylic acid which was then dried to a firm transparent film.

Example II

A developer material consisting of colloiddally dispersed graphite pigment was prepared by dispersing the graphite in a non-conducting petroleum vehicle comprising one part by volume Oildag (a graphite dispersion in petroleum oil supplied by Acheson Colloids Company) to 500 parts kerosene. For fixing the developed image, approximately 5% by weight of paraffin was incorporated in the liquid developer for fixing as by fusing of the paraffin binder on the image surface to bind or hold the graphite development pigment particles more or less permanently into position as deposited under the influence of the electrostatic field conditions.

Example III

Finely ground Epon resin (as commercially available from the Shell Oil Company) was dispersed in Varnolene, in which Epon resin is not soluble, and an electrostatic image was developed on an electrophotographic surface comprising zinc oxide as a photoconductor dispersed in a polyacrylic acid binder matrix. The developed image was fixed by heat fusion or the deposited resin on the plate surface during heat drying and evaporation of the developer vehicle. In this example, since it was desired to emphasize the visible characteristics of the developed image, the intensity and contrast of the image were increased by the lithographic application of an ink. That is, since the surface itself, in non-image areas thereof, has the inherent characteristic of being hydrophylic and since the Epon resin developed image has oleophylic surface characteristics, the required visible intensity was achieved by dampening the entire surface with water and then rubbing a standard greasy lithographic ink thereover with a cotton swab, as a result of which treatment, the ink was repelled by the non-image or undeveloped areas and was received by the image areas on which was the oleophylic fused Epon resin film.

Example IV

For an organosol-type liquid developer agent, one part by weight Saran resin was dissolved in 100 parts mesityl oxide. The organosol was attained by dispersing with stirring one part by weight of the foregoing solution into 20 parts Varnolene, and the electrostatic charge image was developed. After drying the developed plate, the resin image was heat fused for fixing, and the visible image contrast was increased by applying lithographic ink on the fused image as with the previous example.

Example V

For increased visible contrast and intensity, a dye such as Iosol black (commercially available from the National Aniline Division of Allied Chemical and Dye Corp.) was added to the Saran resin solution of Example IV before dispersing the solution in Varnolene. The dye was added in a quantity to give the desired blue to blue-black color,

then the dyed solution was dispersed in Varnolene and the image was developed as with Example IV, with fixing being accomplished by fusing the resin image with heat.

Example VI

As illustrative of fixing the developer material to the plate by softening of the image film surface, a liquid developer was made by dispersing one part by volume of a standard commercial Gravure red ink (identified as IPI-FG-12277) in 500 parts Varnolene. An electrostatic charge image was developed on a plate with this developer and the image surface air dried. The ink pigment was fixed onto the image surface by dipping the developed plate in toluene, a solvent for the binder component of the image surface (in this case an acrylic acid ester polymer known as Acryloid B-7 sold by Rohm & Haas) so that the image surface resin was softened sufficiently to bind or adhere and permanently fix the ink pigment.

Example VII

Using the same liquid developer as in the previous example, an electrostatic charge image was developed on a plate having as the binder component in the electrophotographic surface a methyl acrylic acid vinyl acetate copolymer (commercially available Elvalan resin) instead of the acrylic acid ester of the previous example. After the image was developed and air dried for removal of the Varnolene, the developer material was observed to be fixed onto the image surface. Since Varnolene is not a solvent for the image surface resin, fixing in this case was obtained by the action of the dispersion solvent and/or resin on the image surface film.

Example VIII

The charge image on a plate similar to that in the previous example (i.e., with an Elvalan resin binder in the electrophotosensitive surface) was developed using the organosol dispersion of Saran resin dissolved in mesityl oxide as in Example IV. When the developed plate was dried of the Varnolene vehicle, the image was observed to be fixed on the plate through the action of the mesityl oxide resin solvent with the Elvalan resin in the image surface binder. In this case, the resin was softened under controlled conditions and an equilibrium condition was established before dimensional changes occurred.

While the liquid developer systems above described operate satisfactorily and produce highly desirable results from the standpoint of clarity and definition, other developers have been formulated in accordance with the present invention and constitute improvements and expansions of the systems previously noted. It is to be understood that the principles hereinbelow discussed are equally applicable to some of the developers previously noted.

If a relatively simple dispersion including a carbon pigment dispersed in an oil-type binder or resin and a small amount of thinner is treated with an additional amount of thinner, a point is reached wherein the dispersion assumes a cloudy appearance. Dilution of the dispersion to a relatively low pigment concentration causes the resin molecule to coil up, separate from the pigment, and the pigment agglomerates or flocculates.

With some such dispersions, there is a critical value of dilution wherein the particle or pigment becomes a nucleation condensation point for the resin present in the dispersion in relatively low concentrations, that is, at proper dilution, the pigment becomes a center of activity with respect to any resin present in the mixture and the resin becomes more closely associated with the pigment than with the surrounding medium. The ability of the pigment and the like to behave as a nucleation condensation point is a function of the medium surrounding it as well as other materials present in the medium, for example, charge control and fixing agents. Once the resin becomes more closely associated with the pigment than with the surrounding medium, a new colloidal dispersion

is formed composed of an element carrying with it in preferential association components which may then function as a charge control and fixing agent. It is to be emphasized that the association may result from the formation of a well defined envelope, while on the other hand such an association may be the result of a density distribution of the resin and the like by which high density areas are located in close proximity to the element or particle.

An improved developer composition in accordance with the present invention is a system wherein a marking agent, preferably a pigment, carries a charge control and fixing agent in close association therewith, as has been noted above, and wherein the above components are capable of dilution to a degree suitable for deposition on a surface as controlled by an electrostatic latent image. During such dilution from the original paste-like consistency, there may result a physical relocation of the charge control and fixing agent, and the pigment present in the dispersion is able to function as a nucleation condensation point, as above described.

In accordance with the present invention, a developer includes a suspension medium which surrounds a marking complex which is preferably formed of a marking agent, usually a pigment particle, acting as a nucleation condensation point whereby the charge control and fixing agents are more closely associated with the marking agent than with the surrounding medium. The suspension medium is static with respect to the electrical field present on the substrate while the complex or marking element has electrophoretic properties which provide mobility through the medium. The complex is of a proper small size so as to eliminate any appreciable viscous drag which may interfere with the electrophoretic mobility of the complex. It is preferred that the medium have a resistivity of approximately 10^9 ohm centimeter, or greater. Thus, the medium possesses an electrical resistivity which is sufficiently high so as to maintain the electrostatic latent image in well defined patterns for interaction with respect to the complex or marking element which is to be deposited thereon.

Materials which have been found suitable as a suspension medium include liquids having low vapor pressure, low flash points and low toxicity. The liquid should be chemically stable to the atmosphere while being electrically and thermally stable at ambient atmospheric conditions. Moreover, the liquid should be non-solvent and non-corrosive especially with reference to the film forming binder so as to eliminate swelling, as previously noted, as well as stress cracking or crazing.

The suspension medium preferably includes elements capable of functioning as (1) a diluent or mixture of diluents, or a diluent and a solid which is soluble in the diluent and which is inert with respect to the electrophoretic mobility of the marking element complex, and (2) surfactants present in optimum concentrations so as to control lateral movement of the marking complex as will be discussed hereinbelow.

The complex or element possesses an electrophoretic mobility consistent with the transport time in the developing operation, which is ultimately a function of the processing time. Stated another way, the complex or element should be selected so that it will migrate towards the image bearing surface within the time allowed for development as determined by the time requirements for overall processing. It is preferred that the marking agent include a particle or pigment or other material insoluble in the surrounding envelope, or aggregates thereof, which carry a resin component in close association therewith and charge constituents in sufficient density to form a marking element having a zeta potential consistent with the desired electrophoretic mobility as determined by the transport time associated with the developing procedure, and conditions of the charge image, etc.

The marking agent possesses an inherent electrical charge with reference to its surrounding medium which may be opposite to the charge on the image areas of the image bearing surface. The developer composition itself, however, includes components capable of co-acting with the resin surface of the image bearing member for fixing the marking agents deposited thereon. The envelope surrounding the marking agents preferably includes components such as surfactants and resins which may serve to modify the charge on the marking agents and coact with the resin surface of the image bearing member upon deposition of the marking agents and envelope to fix the agent to the surface once a substantial amount of the suspension medium has been removed.

A satisfactory but less preferable marking agent composition includes the use of a number of different type particles or pigments in a medium so balanced with respect to the mass charge and viscous drag through the medium that the deposition thereof is effected simultaneously within the reference time of the process.

Considering the relationship between a particular medium and a particular marking element, the two are coordinated or correlated so that the fluid viscosity of the medium is such that little, if any, drag is created which opposes the electrical forces giving rise to transient adhesion or secondary fixation as has been heretofore described.

The charge modifying or control agent, as the term suggests, is employed primarily to vary the charges on the marking agent to allow formulation of liquid developers wherein the composite marking element is of the desired charge with reference to the charge on the image areas on the electrostatic latent image. For example, if an electrostatic latent image is formed wherein the image portions are negatively charged, a positively charged marking complex is normally employed for development, and accordingly, the charge modifying agent cooperates with a particular marking agent to provide a positively charged complex which is deposited out of the surrounding medium in accordance with the negative charges making up the electrostatic latent image. In the case of an electrostatic latent image formed of positive charges, the control agent acts to provide a negatively charged complex which is deposited selectively out of the surrounding medium onto the positively charged latent image.

If desired, a charge control agent may be employed which performs two functions, the first being charge control and the second involving the ability of the charge control agent to cause fixing of the marking element on the surface of the image bearing member. While one component may be employed to perform the two functions previously noted, it is to be understood that the two separate components may be employed each of which performs one of the above functions, or two components may be employed which coact to perform the functions above noted.

In discussing the mechanics of the developer formulations, it may be helpful to consider certain principles of surface chemistry, especially those relating to the operation of driers and surface active agents or surfactants. In the simple system of carbon black in carbon tetrachloride, it has been observed that considerable flocculation or agglomeration of the particles occur, and a true stable dispersion of the carbon black is not obtained. If, however, a surface active agent is introduced into the dispersion along with the carbon black, it is observed that a stable dispersion is attained. Such a result is understandable since the surface active agent acts to "wet" the surface of the particle by reducing the surface tension or interfacial tension so as to provide a stable suspension.

Another phase of the mechanics involved in the use of a surfactant relates to the chemical structure thereof. Normally these surfactants are relatively long chain or-

ganic acids for example, oleic, tiglic, lineolenic, linoleic, or naphthenic acids, or the metallic salts thereof such as copper, manganese, lead, zinc, cobalt, nickel, and chromium. In addition to the above, the following operate satisfactorily as surfactants and include octoates, tall oil, phosphoric acid, lecithin, malic acid and the metallic salts thereof, mono-, di-, and tri-ethanolamine, ethylamine and di-, tri-homologs, quaternary organic complexes and other compounds well known in the art.

As the surfactant is introduced into a system containing a dispersing medium and a marking agent capable of functioning as a nucleation condensation point, the surfactant may be absorbed by the marking agent, or it may orient itself such that the cation or anion portion of the surfactant is more closely associated with the agent while the anion or cation portion, respectively, is orientated into the dispersing medium.

As a result of the orientation of the surfactant or the absorption of the surfactant by the agent, the composite of agent and surfactant acquires a characteristic charge which is the same for each composite in the dispersion, and the composite may be conveniently referred to as a marking element. Because each marking element has the same characteristic charge, there is an electrical repulsion between the elements of the dispersion which assists in maintaining it in a stable, flocculation-free state which resembles in physical appearance a stable colloidal dispersion.

The above described three component system including a dispersion medium, a marking agent and surfactant, which latter in effect acts as a charge modifying or control agent, may include components which serve multiple functions as was previously stated. The surfactant in addition to providing a stable dispersion of marking elements throughout the liquid medium may also function as a fixing agent for providing adherence of the marking element to the surface of the image bearing member.

It is preferred in accordance with the present invention that the surfactant be compatible with the image bearing member such that solvating the film forming binder does not occur during contact between the surfactant and the binder.

It is well known that some surface active agents in addition to providing a wetting action and controlling the charge also act as driers promoting polymerization of any resin component having a reactive position. By way of illustration, and in no way to be construed as a limitation on the present disclosure, a marking element including an alkyd resin and a marking agent dispersed in a liquid medium may possess the proper charge characteristics as well as provide a stable colloidal dispersion. Use of such a liquid developer on an image bearing surface may result in a fixing time which is too long for the particular required processing time. In this instance, it may be desired to incorporate a drying agent as a component of the marking element in order to accelerate polymerization of the resin. In such a case, the drying agent cooperates with the other components of the marking element to supplement the charge characteristics of the resin, and thus, the charge on the composite element.

Tests of a system as above described have indicated that as long as the image bearing surface remains immersed in the developer solution, relatively little permanent fixing of the marking element on the surface of the image bearing member occurs, however, as the surface is removed from the developer and excess suspension medium is removed, the marking element exhibits considerable stability with resistance to smudge or smearing.

As was mentioned previously, the surfactant orients itself with respect to the marking agent in a predetermined fashion such that either the cation or anion portion thereof is extended into the surrounding medium. In the case of a highly polar surrounding medium such as trichlo-

roethylene, the aliphatic organic surfactant, exhibits a tendency to dissolve in rather than remain projected into the surrounding medium. The solution of the organic surfactant results because of the polar nature of the medium, and operates to withdraw the surfactant to a position where it is not deposited with the marking agent for coaction with the film forming binder. For this reason, as well as the reasons previously noted, it is preferred to employ a suspension medium which is a non-polar liquid such that the cation or anion portion of the surfactant which projects into the suspension medium is maintained in that condition and capable of coacting with portions of the film forming binder on the surface of the image bearing member.

Typical examples of a developer formulated in accordance with the present invention would include liquids such as Varnolene, mineral spirits or the like, including primarily aliphatic hydrocarbons having a flash point between approximately 100 and 130. The solvent strength of the diluent is preferably between 23 to 40 as determined by the kauri-butanol values and possess an aniline point of about 130 to 190. The diluent may contain about 0.5% water and has a specific resistivity in the order of 10^8 or 10^9 ohm centimeters. Aromatic hydrocarbons generally exhibit an appreciable solvating power due to the presence of unsaturated bonds, or their more polar nature, as is apparent from the fact that they possess a kauri-butanol value of the order of 72 to 110. Accordingly, in employing aromatic hydrocarbons there is an increased tendency for hydrogen bonding to occur resulting in swelling as was previously noted.

Surface active agents which may be employed in addition to those previously mentioned include zinc naphthenate, zinc linalls, manganese oleates, linolenic and abietic acids and salts and mixed salts thereof. A convenient source of pigments of desired small size is a Braden Sutphin ink K-325 (black). To the solvent or diluent there is added approximately 0.5% by weight of a solution of a manganese salt containing 6% metal ion, previously noted, in a suitable diluent. To this mixture is added 0.4% to 1% by weight of the Braden Sutphin black. The above example illustrates the type ingredients employed for a usable developer formulated in accordance with the present invention.

The Braden Sutphin black above described could be considered a toner concentrate for the developer and the following formulations provide a group of resins (other than the Braden Sutphin black above) for satisfactorily formulating a pigment paste or toner concentrate for use in providing liquid developers in accordance herewith. Merely as illustrative:

Example IX

A resin suitable for use in a liquid developer includes kettle boiled linseed oil of Gardner-Holdt viscosity of Z1 to Z4 at 77° F.

Example X

Another such resin is an alkyd resin made up of 60 to 70 parts of mixed linoleic, linolenic fatty acids and about 30 to 35 parts of approximate equivalent molecular proportions of pentaerythritol and phthalic anhydride.

Example XI

A third resin includes an alkyd resin of about 55 to 65% mixed linseed oil fatty acids, the remainder being glycerol and phthalic anhydride in molecular ratios of 1.05 to 1.15 molecules of glycerol per molecule of phthalic anhydride.

Example XII

Another resin includes an alkyd prepared so as to be a hydrocarbon soluble resin of acid value less than 15 and viscosity less than E at 40% non-volatile content when the viscosity is rated in Gardner-Holdt scale at 77° F.

Example XIII

Still another resin includes an oleo resin varnish vehicle comprised of rosin modified phenolic resin and mixed linseed and tung oil in proportions such as to give 70 to 80 gallons of mixed oil per 100 pounds of varnish. The resin is heat blended and bodied at elevated temperatures in excess of 525° F. until the resin oil varnish blend has a viscosity greater than A but less than C at 40% non-volatile content in mineral spirits having a kauri-butanol value equal to 35, the viscosity having been measured on a Gardner-Holdt scale at 77° F.

For the black toners, the marking agent is preferably selected from lamp black, furnace black or the like, having a surface area characterized by the BET method of greater than 40 and less than 80 square meters per gram. Such a pigment has a particle size less than .1 micron average. In this respect, it should be noted that such a small particle, in the proper environment, provides a highly reactive center or nucleation condensation point for attracting the resin or surfactant present in the developer.

A toner concentrate was satisfactorily formulated by taking one of the above resin components and treating such a resin as follows:

Step 1.—The resin is treated at elevated temperatures to a molten state and diluted with 30 to 50 parts of its own weight with varnish, and mineral spirits having a kauri-butanol value of about 35 to 40.

Step 2.—About 2 ounces of pigment were charged into a liter capacity ball mill adding sufficient vehicle (solution of resin from Step 1) to produce a cascading action in the ball mill. Subsequent additions of vehicle (solution of resin) were made as needed particularly to preserve the cascading action since the material thickened during the ball mill operation. When the cascade was stable, the grinding continued until the shading strength became constant. The shading strength was measured by blending one part grinding paste with one part zinc oxide in linseed oil prepared in proportions of 2 parts of pigment grade zinc oxide by weight to one part linseed oil.

Step 3.—When an equilibrium was reached, the grinding paste was diluted with the vehicle (solution of resin as per Step 1) until there was established a pigment binder ratio of about 2.8 by weight of carbon black per 100 parts of resin solids.

Step 4.—To the product of Step 3, was added a solution of drier metals particularly 6% cobalt phthalate, 6% manganese phthalate, and 24% lead phthalate in sufficient proportions to adjust the ratio of metal content to resin solids by weight to approximately 0.5% lead, 0.05% manganese, and 0.05% cobalt.

Step 5.—A blend of 6% manganese linoleate solution in a suitable solvent was prepared so as to provide a mixture of fluid and salts containing 99.5% solvent and 0.5% of the manganese salt.

Step 6.—To 99.0 to 99.6 parts by weight of the blend prepared by Step 5 was added approximately 0.4 to 1 part of toner concentrate. The mixture resulting from this series of steps included a dispersion of finely divided marking elements in a suitable suspension medium. Such a dispersion as prepared above operates quite satisfactorily as a liquid-developer in electrostatic photography with the advantages as previously noted.

As illustrative of other satisfactory pigments for use in accordance herewith, the following may be noted: organic bentonites, bone black, charcoal black, mineral and iron oxide black varied in percentages so as to provide a surface area corresponding to the surface area of the pigments referred to above. As illustrative of color toners for use herewith pigments such as azo yellow having a pigment concentration of about 15%; cyanine (blue) phosphomolybdenic toner, about 12% pigment concentration, magenta (red) phosphomolybdenic toner 12 to 15% pigment concentration, with a ratio of pig-

ment to resin solvents as noted above in connection with the black toners.

Other pigments which have been found suitable in accordance with the present invention include antimony vermilion, barium yellow, blue verditer, bone black, cadmium red and yellow, cerulean blue, charcoal black, chrome green and yellow, cobalt green, blue violet and yellow, Egyptian blue, emerald green, black and red iron oxide, manganese blue and violet, titanium dioxide, zinc oxide and carbon black. It is preferred that the above pigments be of a size in the order of 0.01 to 40 microns and preferably in the range of 0.01 to 5 microns in order to provide fine "grain" image.

INTERACTION OF THE LIQUID DEVELOPER WITH THE FILM FORMING RESIN

If an electrostatic latent image is formed on an image bearing surface in any of the conventional methods heretofore employed, differentially charged image and non-image areas are present on the surface of the image bearing member having a configuration substantially identical to that of the developed image. During development the marking elements are desired to be deposited on the image areas, and only the image areas, and remain thereon as a permanent or at least substantially permanent deposit formed on the surface of the image bearing member in image configuration. To this end, the developer includes a suspension medium having dispersed therein a finely divided agent, and preferably a pigment which carries in preferential association therewith a resin and/or surfactant.

The marking agent is present either in the form of a pigment or other particle surrounded by an envelope of resin and/or surfactant, or clusters of individual particles surrounded by an envelope of resin and/or surfactant. The complex element, that is, the marking element above described carries an appropriate charge which has a polarity such that it is capable of being attracted to those portions of the image bearing surface which have been defined as the image areas.

As the complex or the marking element, as above described, comes into contact with the image bearing portion of the image bearing surface, one of two things may occur. If, in the presence of the thinner there is no tendency of the envelope to wet the coating, the complex will be deposited on the paper as a unit and generally retain the shape it had in the developer dispersion, and may be easily dislodged resulting in smearing and loss of definition. On the other hand, if the wetting ability of the complex for the surface is strong enough, the envelope surrounding the particles or clusters partially flattens out or spreads on the surface. If it be considered that the internal angle between the surface of the paper and a line tangent to the surface of the complex at the point of contact with the base is theta, then with an increase in time the theta angle decreases as the resin continues to deform due to the wetting ability of the complex with respect to the binder. In a relatively short time, the complex flattens out until a condition is reached wherein the van der Waal's forces attract the components of the complex to the surface of the film forming binder. At this point, the resin envelope covers the marking agent causing it to adhere to the film forming binder in a semi-permanent transient condition. Additionally, the transient condition is characterized by an attraction between the charged complex and the image area, and tests have indicated that while in contact with the developer medium, some marking elements in accordance herewith may be removed by brushing them off although there remains on the surface a considerable quantity of marking elements retained thereon in image configuration.

As a substantial amount of the suspension medium evaporates or is otherwise removed, the resin and/or surfactant of the complex coalesces and is polymerized

to cause substantially permanent cohesion and adhesion of the marking element to the surface of the film forming binder. Since the theta angle has decreased, due to the wetting ability of the resin envelope for the resin film forming binder, the electrical charge condition of the binder molecules acts on the pigment or aggregates thereof to attract the same to the surface of the film forming binder. Accordingly, the pigment is virtually covered by a layer of resin which causes it to remain permanently adhered to the image bearing surface.

The wettability of the complex towards the image bearing surface should be at an optimum value so as to provide a controlled lateral mobility along the surface of the film forming binder. If the complex is not capable of wetting the surface upon which it is deposited, the desirable secondary effects and fixing previously noted will not be achieved, and the marking element may be dislodged quite easily. On the other hand, the wettability and flow of the complex should not be so great as to cause excessive lateral spreading since this interferes materially with the resolution of the final print. Employing developers and image bearing members coordinated in accordance with the present invention, resolution in excess of 100 lines per millimeter has been achieved.

As the image bearing member is withdrawn from contact with the liquid developer, there remains on the image bearing surface a relatively thin film of the suspension medium as well as the marking elements which have been deposited in image configuration, as above described. The very thin film of the suspension medium should be substantially removed to provide a virtually dry print. In accordance with the present invention it is possible to use a squeegee roller in providing removal of considerable amounts of the suspension medium without effecting removal of significant amounts of the marking elements from the image portions of the image bearing surface.

As was stated previously, providing a suspension medium which is non-polar and a film forming binder which is polar represents an optimum condition. As a corollary to this, the squeegee roller is formed with a non-polar surface material exhibiting electrical characteristics comparable to that of the suspension medium. This represents an optimum condition since the dispersion and image deposit are stable with respect to the roller. Additionally, if the resin envelope of the marking complex is stable, it splits away from the roller at a low shear level characteristic of the suspension medium to eliminate any viscous drag between the roller and the deposited resin envelope. By employing a roller material which is non-polar, the formation of ghost images on the squeegee roller is substantially eliminated, and thus, a squeegee roller may be employed to remove significant amounts of the suspension medium without materially interfering with the marking elements deposited out of the developer.

Another advantage attributable to a squeegee operation may be understood with reference to "multi-down" or polychromatic work wherein multi-colored images are to be formed, as will be described hereinafter. The application of pressure by the squeegee roller operates to compress or coalesce the deposited resin envelope to a substantially uniform thickness so that penetration of light necessary for the formation of charge images representative of the different colors will be uniform in those areas covered by a resin envelope. Thus, it can be seen that the use of a squeegee which does not remove significant amounts of the deposited marking elements and which operates to compress the resin envelope to a uniform thickness may be employed advantageously in polychromatic or multi-color work.

MULTI-COLOR PRINTS BY ELECTROSTATIC PHOTOGRAPHY

The compatibility of the film forming binders, mentioned above, in the presence of a liquid developer compounded as previously described is extremely advanta-

geous when considered in reference to polychromatic work wherein an electrophotographic process is employed for producing multi-colored prints. As has been stated, the marking element above described when deposited on the image bearing surface remains thereon in substantially permanent fashion due to polymerization of the resin or combination of resin and surfactant, or due to the reaction of a component of the developer with a component of the film forming binder.

The unusual stability achieved by the combinations above described readily lends itself to a system wherein a series of electrostatic latent images are formed each representative of a different color, and wherein each image is developed by a liquid developer of appropriate color to produce a multi-color print. As will be hereinafter described, the steps involved in forming a multi-color print include forming a first image, developing that image, forming a second image in registry with the first and having a charge configuration representative of a second color and developing that color, and so forth, until a multi-color image is formed. During the development of each of the images, the marking elements deposited in the previous development step are exposed to the suspension medium but are not adversely affected thereby since the marking agent is permanently adhered to the surface, as above described.

By the polychromatic system of this invention, a transient fixation of the marking element is achieved, as previously noted, and therefore it is possible to form and develop a series of images without the additional step of separately fixing each image after development thereof. Additionally, due to the compatibility of imaging materials, the image bearing surface is unaffected by repeated contact with the suspension medium previously described.

A singular and noteworthy advantage of the color technique of this invention lies in the fact that the marking elements carry or are accompanied by components capable of causing self-fixing of the marking agents to the surface of the image bearing member, and accordingly, those portions of the surface wherein there is no deposit of marking elements retain the electrical, physical as well as chemical properties they had originally. Moreover, by control of the material constituting the film forming binder as well as the components of the developers, background deposits are substantially eliminated thus maintaining background free of deposits which may interfere with subsequent developing operations.

All of the above advantages are of considerable importance in forming a print in a single color, and as will be apparent, the several advantages above enumerated are of even greater importance in multi-color work wherein the image bearing surface may be treated with as many as six or seven sequential developing operations to provide a print of six or seven colors.

It should be noted that the liquid developer and the film forming binder, if coordinated properly as above described, provide a compatible system wherein the image bearing surface retains remarkable dimensional stability in addition to substantial reduction in undesirable secondary effects, previously noted, thereby allowing repetitive contact between the image bearing surface and a suitable liquid developer for multi-color work without materially interfering with the characteristics of the image bearing surface or the definition, contrast, etc., of the deposited image or images.

SINGLE COLOR SYSTEM AND APPARATUS

A system incorporating the above advantageous relationships previously described may be understood with reference to FIG. 1 which illustrates in schematic form apparatus embodying and for practicing the present invention. A roll of photoconductive paper or the like indicated at 12 as representing a continuous web of paper or other suitable base material is provided with a suitable electrophotosensitive surface layer of the type de-

scribed in the copending application Ser. No. 640,353, previously mentioned. From the roll 12, the web 14 is withdrawn for feeding through the machine, as for example, by passing over a guide roll 15. A registration punch 16 or similar device for controlling or metering the feed of web 14 in increments commensurate with the linear dimension of whatever image is desired to be produced on the surface of the web 14 cooperates with a web length measuring roll 18 for controlling feeding of the web 14, either incrementally or continuously through the apparatus. A registration mark reader and imaging control 19 acts as a further component of the web feed control elements of the apparatus.

In the apparatus illustrated in FIG. 1, the electrophotosensitive or photoconductive surface is on the inside surface of web 14 (i.e., the lower surface of the horizontal portions of web 14) and this electrophotosensitive surface is given a uniform charge by a corona unit 20 through which the web passes. Positioned in close contact with the reverse side of the web 14 directly opposite the charging unit 21 is grounded a metallic plate 22 which is of some assistance in providing a uniform charge on the surface of web 14. After leaving the corona charging unit 20, the electrophotosensitive web with a uniform electrostatic charge pattern thereon passes into the exposure area of the machine indicated at 23 where a light image 24 is projected onto the web as by a projector 25 having lens elements 26, and condensers 27 for a source of light 28 for projecting the light image 23, for example, a photographic transparency indicated at 29. The light source 28 is preferably of the flash exposure type so as to provide a high level of illumination in a relatively short time thereby facilitating operation on a continuous basis, since the transparency may be flashed in a short interval of time rendering it unnecessary to maintain the web stationary during the flashing operation. The projection of the light image 23 onto the charged surface of web 14, of course, alters the uniform electrostatic charge therein which was produced by the corona charging unit 20, and produces on the web 14 a latent electrostatic charge or pattern including differentially charged image and non-image areas.

Immediately after exposure to this light image, the web 14 is advanced to a developing station generally indicated at 30, and the web passes over an insulating guide roll 32 and around a driving capstan 34 which immerses the image and non-image areas of the web 14 in a liquid developer composition 35 contained in a developer tank 37, wherein development of the electrostatic latent image on web 14 occurs in accordance with the principles of this invention. Still driven by a driving capstan 34, the web 14 continues over rolls 39 and 40, to contact a heated drying drum 42 around which web 14 travels for the drying removal of the suspension medium allowing the marking elements to remain substantially permanently adhered on the surface of the web. Thereafter, the web 14 leaves the drier, passes over guide roll 44 and onto a sheeter or other apparatus for subsequent operations. A hood 45 is preferably provided around the drying drum 42 with a suction vent 46 to aid in the evaporation and removal of volatile components as the web passes around drying drum 42.

If desired, the developing station may include a counter-electrode, or development electrode of the type described in application Ser. No. 762,756 previously mentioned or a liquid counter-electrode of the type described in copending application Ser. No. 96,436, filed Mar. 17, 1961 now abandoned.

It is preferred that a squeegee roller be employed to remove significant amounts of excess suspension medium which adheres to the surface of the web 14 which has been treated with a liquid developer. The details and operation of the squeegee roller will be discussed more fully hereinbelow in connection with the multi-color system.

MULTI-COLOR SYSTEM AND APPARATUS

Production of multi-color prints in accordance with the present invention may be understood with reference to FIG. 2 which illustrates apparatus embodying and for practicing the present invention. A roll of photoconductive paper, or the like, indicated at 50 as representing a continuous web of paper or other suitable base material is provided with a suitable electrophotosensitive layer of the type described in copending application Ser. No. 640,353, previously mentioned. From the roll 50, a web 52 is withdrawn for feeding through the automatic web tensioning device generally indicated at 55 including guide rolls 57 and floating roll 58 for maintaining the unwind tension constant, and infeed rolls 59 which act to meter the web entering the machine so as to maintain a constant and uniform web tension throughout the travel therethrough. The web tensioning control unit 55 is of conventional design and operates to maintain the web centered during treatment as well as maintaining the proper tension on the web as it passes from station to station. The web control system may also be used for controlling feeding of the web 52 either incrementally or continuously through the apparatus as will be described more fully hereinbelow.

The first operation involved in forming a multi-color print takes place at the first station wherein the surface of the image bearing member is charged to a uniform potential, as is well known in the art. This is accomplished by passing the web over roller 61 and through a corona unit indicated at 65 which is of a type well known in the art. A conventional adjustable power supply may be provided for establishing a relatively fine balance between the corona currents for providing an optimum charge condition on the surface of the paper. The electrophotosensitive, photoconductive surface or image bearing surface is on the inside surface of the web 52 (i.e., the lower surface of the horizontal portions of web 52), and as the paper is advanced from the first charging station 65 to the first exposing station generally indicated at 67, a light image 68 is projected onto the image bearing surface by a suitable projection unit 70.

The projection unit may, if desired, include a variable magnification feature, and includes a flash tube capable of, for example, four 160 watt second flashes per second. During this exposure operation, an electrostatic latent image is formed having an image configuration of the first of a series of colors which will ultimately comprise a multi-color print. In addition to an electrostatic latent image representative of a particular color, there is also formed an electrostatic latent image representative of an index mark which serves as a reference mark for actuating the projection units in the subsequent stations, as will be more fully described below. The index mark is preferably formed along or near the margin of the web in a predetermined relation to the color image thereby providing a convenient reference mark which may be used to orient the several images with respect to each other and in proper relationship in accordance with the final multi-colored print.

Subsequent to the exposure of the first of a series of electrostatic latent images, the web 52 carrying the first electrostatic latent image is advanced to the first developer station 75 of a series of developer stations. The image bearing member carrying the electrostatic latent image in color configuration and an image of the index mark is advanced over an insulating roller 76 and between a pair of rollers 78 and 79 at which point the image bearing surface is treated with liquid developer contained in the tank 80, or other suitable container. Positioned in relatively close relationship to roller 78 is a squeegee roller 82 which operates to remove substantially all of the suspension medium adhered to the surface of the web 52.

The web carrying the developed image is then passed over rollers 83 and 84 to a second station including charging unit 90 wherein the web is given a second uniform

charge by a corona unit similar to that previously described. As the charged web is passed around insulating roller 92, it enters the second exposure zone generally indicated at 95, and as the index mark moves past the photo-electric register control 96, the second projection 98 is energized to expose the charged image bearing member to a second image having a configuration representative of a second color, and properly registered with respect to the first image. The photoelectric register control is capable of reading to within ± 0.0005 inch to produce a pulse which is fed to an amplifier providing a suitable output for control of the flash tube contained within each projection.

In similar fashion to that above described, the web is advanced to a second developing station 100 which contains the same elements as does station 75 with the exception of the liquid developer which is of the desired color in accordance with the configuration of the electrostatic latent image formed in the second exposure zone.

In this manner, the web is advanced in succession through a third station including a third charging unit 102, and thence to an exposure zone 105 wherein the index mark is recognized by the second register control 107 to trigger the third projection unit 109. In the third developing station 110 containing the same elements as described in connection with developing stations 75 and 100, the third electrostatic latent image is developed in a third color, and thereafter the web is advanced to a fourth station generally indicated at 115 including a charging unit 117, an index register unit 118 which controls operation of the fourth projection unit 120. The web carrying the fourth electrostatic latent image is advanced to the fourth developing station 122 wherein the fourth electrostatic latent image is developed as described in connection with the three preceding images.

The last station 125 includes a charging unit 126, an index register unit 127 for triggering the projection unit 129, and a developing station 130 for developing the fifth electrostatic latent image in a manner described in connection with the first electrostatic latent image. As the web having the multi-colored image deposited thereon leaves developing station 130, it is advanced over a cutoff compensator roller 135 and advanced between pull rolls 136 to a sheeting assembly 140 including a cut-off control 141 at which point the web is severed to provide individual multi-colored prints. The sheets are advanced into a stacking assembly generally designated 145 which delivers the individual sheets to a delivery unit 148. If desired, an exhaust hood 150 may be provided for removing any odor which may be present due to the nature of the liquid developer or any constituent thereof.

It is desired at each exposing station that the web follow a slightly curved image path or be pulled across and in contact with a surface for substantially eliminating transverse vibration and curling. Additionally, the apparatus may be operated in a continuous or incremental manner to provide duplicate copies of the same multi-colored print or copies of different multi-colored prints, depending on the need.

Each of the projection units 70, 98, 109, 120 and 129 is provided with a transparency or microfilm having an image thereon representative of the image in each color so that during the first exposure, an electrostatic latent image is formed corresponding to the red portions of the final print, for example. In similar fashion, the second, third, fourth and fifth units may contain transparencies capable of providing images corresponding in configuration to the yellow, blue, green and black portions of the final print so as to provide a multi-colored image including the colors red, yellow, blue, green and black, for example. It is to be noted that the image on the transparencies or microfilm need only be in black and white since the color of the particular image is determined by the color of the developer. It is to be understood that the sequence of depositing the colors as well as the combination of colors may be varied in accordance with the par-

ticular need, and the above colors are cited by way of illustration only and are not to be construed as a limitation upon the present invention.

It is also possible in accordance with the present invention to overprint or deposit one color on another to form a third color. In this mode of operation an electrostatic latent image is formed having a configuration representative of a first color, and is developed in a first color. Thereafter a second electrostatic latent image is formed which overlaps at least a portion of the first developed image, and the second image is developed in a second color. The overlapping portion of the two images is of a color different than the first and second color. For example, yellow may be overprinted with magenta to give a red in the overprinted areas, or yellow may be overprinted with Cyan to give green in the overprinted areas, etc. As the second developer is deposited in contact with the first, the marking elements of the second developer coact with the deposited elements of the first developer and operate to maintain the second deposited elements substantially permanently adhered to the first and to the surface of the image bearing member.

In a continuous operation, the frequency of exposures at the first station is programmed or otherwise arranged to form a given number of electrostatic latent images per unit length of the web. The formation of each of the subsequent images is controlled by the index or reference mark formed during each of the first exposures, and thus apart from the programming at the first station, the system is automatic. Additionally, it is also possible to employ an arrangement wherein the projected image is of a size smaller than the length of web at a particular exposure station. This may be accomplished by employing a transparency or the like having opaque shielding portions, or light shields masking out the unexposed portions of the web at each exposure station.

By a suitable control system, well known in the art, the programming of the rate of exposures at the first station may be controlled in order to maintain the distance between repetitive images at a minimum. Formation of an index or registration mark at the first station operates automatically to trigger the flash tube at each station as the photocell senses the mark. As a result of this mode of operation, it is possible to form images having a width corresponding to the web width and of any length up to the length of web at each exposure station while maintaining the amount of unexposed paper between and around the images to a minimum.

It is of course understood that the exposing portion of each station is constructed so as to prevent light in the remaining stations from being introduced into any particular station, and thus spurious images resulting from extraneous light are avoided. An especially noteworthy advantage of the system relates to the continuous tone printing in one or more colors. An electrostatic latent image may be formed from a continuous tone transparency or a continuous tone reflect copy by procedures individually well known in the art. The image areas on the surface of the image bearing members have a charge density which varies in accordance with the density of the image of the continuous tone transparency or reflect copy. The quantity or density of the marking element deposited on the electrostatic latent image varies in accordance with the charge density to form a continuous tone image wherein the color density corresponds to the color density of the original. Additionally, by overprinting a continuous tone it is possible to provide a full-color or multi-colored continuous tone print.

If desired, single prints each having different patterns of each of a given number of colors may be produced by operating the device shown in FIG. 2 in such fashion that the transparencies representative of various color configurations are automatically and sequentially presented to the exposure units in the proper order. Additionally, it is also possible to form only a two color print

even though the image bearing surface may be moved through five stations and this may be conveniently accomplished by, for example, disabling the charging units at those stations in which no image formation is to occur. Additionally, the roller at each station corresponding to roller 78 may be urged out of its normal position with respect to roller 79 such that the web is not treated with developer. Alternately, the developer may be drained from the stations which are not to be used. Due to the nature of the developer and image bearing surface, as above described, background deposits will be maintained at a significantly low level if not entirely eliminated.

As was previously noted, a registration unit is positioned in the stations other than the first station for providing predetermined orientation of the subsequently formed images with respect to the first formed image. Registration may be conveniently accomplished by aligning the exposure units properly with respect to the web travel and reading the position of the index mark by the photocell detectors positioned in the path of web travel along that portion of the web at which the index or registration mark is formed. To accomplish reading of the index mark, a low intensity bulb preferably of red light is positioned in each station so as to provide a light source capable of rendering the index mark visible to the photocell, and which does not interfere materially with the illumination generated by the flash source.

Since a red light may be employed for detection of the index mark, it is preferred as a practical matter to deposit the red color if one is required, at any station other than the first station. The reason for this will become apparent if one considers that if the index mark were red on an image bearing surface having a white background, the index mark when exposed to red light would be indistinguishable from the background and therefore incapable of detection by the photocell. Accordingly, if a red color is to be deposited, it is preferred to have the red color deposited in any order except the first, in order to facilitate reading the index mark which may be illuminated by red light. In the alternative, if the index mark is red, a low level violet or ultraviolet light may be employed which does not materially interfere with the formation of the electrostatic latent image and which is capable of illuminating the registration mark to enable recognition by the photocell unit in any particular station.

As was previously discussed, the liquid developers of the present invention include components which are compatible insofar as the film forming binders are concerned, and therefore, the ancillary and secondary effects previously noted are substantially eliminated in order to maintain background deposit at a minimum.

The development techniques as well as the operation of the squeegee drying system may be more clearly understood with reference to FIG. 3 which shows, in schematic form, the basic elements included in the developing station as shown for example in FIG. 2, and which may be employed with the single color apparatus shown in FIG. 1. A suitable image bearing member 150 of the type previously described having an electrostatic latent image formed on the image bearing surface 151 thereof is advanced to the developing station by suitable means discussed above in connection with FIGS. 1 and 2. Liquid developer 153 contained in a tank or other suitable receptacle 154 has at least partially immersed therein a developer roller 155 spaced from an idling roller 156 to define a generally horizontal nip 157 therebetween having a predetermined nip size.

The developer roller is arranged with respect to the receptacle 154 and the developer 153 contained therein so as to dip into the same and carry, the developer into contact with the surface 151 bearing the electrostatic latent image as it is advanced between the nip 157. The roller 155 may be of insulating or conductive material and may function in one of two ways depending on the predetermined size of the nip 157. If the size of the nip

157 is less than the thickness of the image bearing member 150, the developer roller operates on a pressure principle which progressively brings the marking complexes into close contact with the image bearing surface, and as a portion of the image bearing surface is positioned at the point of minimum separation between rollers 156 and 155, a slight pressure is applied to urge the marking elements deposited in image configuration forcefully onto the surface of the image bearing member.

During downward movement of the roller, after contact with the image bearing member, the marking elements not deposited on the image bearing surface are redistributed through the developer due to the rotational velocity of the roller 155 with respect to the body of developer. The developed image is present in the area indicated generally at 160, and is progressively advanced to the squeegee roller 165 positioned relative to the roller 156 so as to define a generally vertical nip 167 therebetween. Positioned between the roller 156, the image bearing surface and the squeegee roller 165 is doctor blade 169 which projects into the nip 167 and whose surfaces 170 and 171 are spaced a relatively small distance from the surface of the image bearing member 150 and the outer surface of roller 165.

The size of the nip 167 is preferably such that it is less than the average thickness of the image bearing member 150 so that the roller 165 is maintained in intimate contact with the image bearing surface and applies pressure to the moving image bearing member to squeegee away substantial amounts of the suspension medium which remain adhered to the surface of the member 150. In order to prevent accumulation of the suspension medium in the nip 167, the doctor blade 169 is positioned as above described and arranged so that the lower portion thereof is in contact with the body of developer. In this manner, any significant amounts of suspension which tend to accumulate at the nip will be removed, as formed, and conducted along the surfaces of the doctor blade 169 to the body of developer 153.

An alternate mode of operation of the developing station shown in FIG. 3, involves the use of a developer roller 155 positioned with respect to roller 156 so as to define a generally horizontal nip 157 having a nip width slightly greater than the average thickness of the image bearing member 150. In this arrangement, the roller operates as an intermediate to apply liquid developer to the surface bearing an electrostatic latent image and does not apply pressure as was the case with the arrangement previously described wherein the nip width is slightly less than the average thickness of the image bearing member. Regardless of the mode of applying the developer to the image bearing surface, the operation of the squeegee roller is the same as that previously described.

As was described above, the squeegee roller is preferably constructed of a material which exhibits electrical and polar properties similar to that of the suspension medium. A roller constructed of vulcanized linseed oil or various synthetic rubbers have been found to operate satisfactorily, and as a general rule, any resilient material which is unaffected by the suspension medium or components of the developer may be utilized.

The enhanced advantages of a multi-color system, and of a squeegee system obtainable in accordance herewith are best realized by properly coordinating the nature of the film forming binder with the components of the developer. In a multi-color system of the type above described, wherein an image bearing surface is successively charged, exposed and developed by liquid developers of different colors, the stability of the film forming binder, and therefore the stability of the image bearing surface is directly related to the interaction between the components of the developer and the surface of the image bearing member. Providing a system of electrostatic photography wherein the developed image remains substantially fixed on the image bearing surface is in itself a highly desirable goal. Additionally, the use of a developer which becomes

substantially fixed to the image bearing surface and is thereafter unaffected by repeated contact with a second or subsequent liquid developer is highly advantageous in multi-color systems wherein a first depositing image may be exposed to as many as ten subsequent developing operations.

As can be understood, care must be taken to avoid background deposits which may interfere with subsequent exposure and developing operations, and in this connection, it is pointed out that the reduction or substantial elimination of the secondary effects such as viscous entrapment, and the like, previously noted operate advantageously to maintain such background deposits at a uniform low level. Moreover, the control of the electrical and chemical phenomena taking place at the interface of the image bearing surface and the developer, and especially the ability to create a condition in which marking elements are maintained, at least initially, in a semi-permanent transient state on the surface of the paper advantageously allows the use of a squeegee roller system which not only removes a substantial amount of the suspension medium to allow polymerization of the resin component of the marking element, but also allows the use of a squeegee system which compresses the resin envelope to a substantially uniform thickness on the surface of the image bearing member thereby allowing formation of subsequent images wherein the penetration of light onto the electrosensitive coating or other suitable base member is uniform in nature.

In accordance with the present invention, contamination or carry over of developers has been substantially eliminated by controlling electrical and chemical conditions at the developer-image bearing surface interface so as to eliminate, to a great degree, viscous entrapment of marking elements which may become redistributed in a second developer. Even if some marking elements were to be deposited, the fact that the elements include resin components capable of being polymerized, and thus insoluble in the suspension medium, provides another convenient way of preventing carry over of one developer into subsequent developer stations.

The system above described offers the advantage that the components of the developer composition and the resin surface of the image bearing member are coordinated and correlated to provide maximum stability of the resin surface during periods of repeated contact with the several developer compositions employed in multi-color work.

If desired, a counter-electrode or developer electrode may be employed which coacts with the field present as a result of the electrostatic latent image to effect substantial elimination of halo or edge effect and to increase the rate of marking element deposition. An example of a counter-electrode which may be employed is one of the type disclosed in copending application Ser. No. 96,436, filed Mar. 17, 1961 above identified, application Ser. No. 762,756, filed Sept. 23, 1958 and application Ser. No. 762,699, filed Sept. 23, 1958.

Moreover, various methods may be employed for forming an electrostatic latent image, for example, devices wherein an electrostatic latent image is formed directly on an insulator without necessarily involving the steps of uniformly charging and exposing. Such systems are individually well known in the art.

The system above described constitutes a much improved system of electrostatic photography due to the fact that the developer is "self-fixing," and equally as important is the fact that the image is formed and developed on an image bearing member which remains dimensionally stable in the liquid developer. As a result of the stability of the electrosensitive member including a film forming binder with the components of the liquid developer, it is possible to form multi-color images by the procedure above identified.

While the methods and forms of apparatus herein described constitute preferred embodiments of the invention,

it is to be understood that the invention is not limited to these precise methods and forms of apparatus, and that changes may be made therein without departing from the scope of the invention which is defined in the appended claims.

What is claimed is:

1. A process for sequentially forming a plurality of images on an image bearing member including an image bearing surface comprising the steps of sequentially forming a series of electrostatic latent images on said surface, sequentially developing said images after formation thereof with a liquid developer, each liquid developer including marking elements dispersed in an electrically insulating suspension medium, said marking elements of each developer including a liquid resin material for substantially adhering to said surface upon removal of said suspension medium, the suspension medium of each said developer being substantially free of resin material other than that associated with the said marking elements so that resin material from the said developer is deposited essentially only where said marking elements are deposited, removing the suspension medium adhering to said image bearing member after each development operation to cause substantially permanent adhesion of the marking elements deposited during the said development operation, and drying said image bearing member after the last development operation.

2. A process as set forth in claim 1 wherein each said developer is of a different color.

3. A process as set forth in claim 1 wherein each said latent image is of a different configuration.

4. A process as set forth in claim 1 wherein at least a portion of at least one of said images overlaps at least a portion of some other image, said one and said other images being developed by two different colors, and said overlapping portion of said images being different in color from said two different colors.

5. A process as set forth in claim 1 wherein at least one of said images is a continuous tone image, and wherein the marking elements of the developer used for development thereof is deposited under the control of said continuous tone electrostatic latent image.

6. A process as set forth in claim 1 wherein said image bearing member includes a surface composed in part of

a polar polymeric material and wherein the suspension medium of said developer is non-polar in nature.

7. A process as set forth in claim 1 wherein said image bearing member is in the form of a web, and wherein the portion thereof being developed is in facing contact with a developer while the opposite surface thereof is in contact with a roller.

8. A process as set forth in claim 1 wherein said suspension medium is removed by pressure-contacting the image bearing member with a rotating roller travelling at the same linear speed and in the same direction as said image bearing member.

9. A process as set forth in claim 1 wherein said image bearing member is a web maintained under tension, and wherein the surface of said web opposite the image bearing surface is maintained dry during development by contacting the opposite side with a roller.

10. A process as set forth in claim 1 wherein the image bearing member is a web and wherein said process includes the further steps of forming an electrostatic latent image of a registration mark simultaneously with the formation of the latent image of the original during the first exposure operation, developing both said latent images, detecting said registration mark in at least one of said subsequent image formation operations, and forming at least a second image in registry with the first as controlled by said registration mark.

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