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ELECTROSTATIC PHOTOGRAPHY SYSTEMS

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ABSTRACT OF THE DISCLOSURE

A liquid organosol or emulsion developer composition for latent electrostatic images is disclosed which comprises an insulating carrier liquid having a KB value of between 20 and 100, pigment particles which form an association complex with two different resins both insoluble in the carrier liquid, one of the resins being a halogenated resin.

This application is a continuation of application Ser. No. 420,449, filed Dec. 22, 1964 which in turn was a continuation-in-part of application Ser. No. 288,610, filed June 18, 1963, both now abandoned, and assigned to the same assignee.

This invention relates to electrostatic photography and more particularly to an improved negatively charged liquid developer, and the method of using the improved developer to develop an electrostatic latent image on an electrically insulating surface.

It is a primary object of the present invention to provide a negatively charged liquid developer for use in electrostatic photography.

The above object as well as those hereinafter specified has been achieved by taking advantage of what heretofore has been a disadvantage, namely, the tendency of certain materials to flocculate or agglomerate into clumps when used in a liquid developer.

The cause of flocculation between particles has been treated extensively in textbooks dealing with dispersants, and while the exact cause of flocculation is not known, it is known that as the particle size decreases the tendency towards flocculation increases, and thus if an attempt is made to achieve high resolution by utilizing relatively small particle sizes, there may well be an increased tendency towards flocculation. While dispersants could be used to break up or separate the particles, the efficiency of the dispersant is related to its ability to create an electrostatic charge around an individual particle which would tend to repel it from another particle. Any source of charge carriers, such as dispersants and low molecular weight materials impairs the efficiency of the developer since charge carriers are then present in the mixture and may destroy the charge image itself or create a condition within the body of the developer which ultimately prevents migration of the developer particle toward the electrostatic latent image, if one still exists.

This invention utilizes the tendency of fine particles to flocculate and controls such flocculation as a means whereby high contrast negatively charged developers may be provided while retaining the order of resolution possible with a given image surface and a developer wherein the color source is of micron or sub-micron size. Generally speaking the developers of this invention are preferably self-fixing by any one of several mechanisms to be described in more detail hereinbelow, and for the present discussion reference will be made to only one of those mechanisms, i.e., fixing by evaporation or removal of the carrier, suspending or continuum liquid of the developer.

The developer composition of the present invention includes an electrically insulating liquid in which is dispersed a multiplicity of negatively charged marking elements, each marking element in turn being composed of an association complex including a first resin which is halogenated, and an envelope substantially completely enclosing the complex and formed by a second resin, and the composite or marking element carrying a negative charge for attraction and deposition on an insulating surface as controlled by the charges of the electrostatic image. The marking element constitutes the dispersed phase of what may be considered to be an emulsion or organosol wherein the outer resin envelope is insoluble in the carrier liquid. The association complex includes a halogenated resin and a multiplicity of marking particles which have been drawn together by their inherent tendency to flocculate, or by the tendency of the marking particles to flocculate in the presence of another material such as the first resin. Thus, there is provided an inner core composed of particles having a relatively small size whereby reasonably high resolution may be achieved while at the same time achieving a contrast which is increased over that which could be achieved merely by providing a stable dispersion in which the same marking particles are maintained in a non-flocculated condition and deposited under the same conditions.

The first resin, which is halogenated and preferably chlorinated, is characterized by its tendency to flocculate in the presence of a thinner which is preferably a non-polar electrically insulating liquid having volume resistivity sufficiently high to prevent discharge of the electrostatic latent image, for example about 10^9 ohm/centimeter, or higher. Such thinners are characterized by relatively low Kauributanol values which permits flocculation of the first resin upon dilution with the thinner. Basically, the first resin is compatible with the thinner up to predetermined relative proportions of thinner and resin wherein the viscosity of the mixture is relatively high as compared to the viscosity of the thinner. Above predetermined relative proportions, the resin is not compatible with the thinner and forms a flocculate and the viscosity of the mixture is close to the viscosity of the thinner.

The first resin may be a liquid per se, or a solid resin in pure form and dissolved in a relatively small amount of a polar solvent or thinner of relatively high KB value, and the resin and solvent are so coordinated and correlated that the solvent does not subsequently function as a contaminant, and the combined characteristics of resin and solvent are such that the resin is capable of forming a flocculate when the solution is diluted with the thinner of the above type to a concentration wherein the liquid resin is not compatible with the thinner.

The second resin, which is a liquid, is characterized by a decreasing solubility with increasing concentration of a thinner of the type above described, and its ability to provide an organosol or stable suspension of non-flocculated colloidal particles when in the presence of the thinner. Again, the second resin is compatible with the thinner up to predetermined relative proportions of thinner and second resin wherein the viscosity of the mixture is relatively high as compared to the viscosity of the thinner. Above the predetermined relative proportions, the second resin is not compatible with the thinner and unlike the first resin, the second resin forms a stable organosol of dispersed particles rather than a visible flocculate or sedimentary precipitate in which the viscosity of the organosol is close to the viscosity of the thinner.

Here too, the second resin may be a liquid per se or a solid resin in pure form and dissolved in a relatively small amount of a suitable solvent such as for example a polar solvent or thinner of relatively high KB value,

and the second resin and solvent are so coordinated and correlated that the solvent will not subsequently function as a contaminant, and the combined characteristics of the second resin and the thinner are such that they are capable of forming an organosol when diluted with the thinner of the above type to a concentration wherein the second liquid resin is incompletely soluble in the thinner. Preferably the first and second resins are present in an amount sufficient to form the association complex and the outer resin envelope as previously described.

The marking particles which form a color ingredient of the association complex are preferably pigments which are insoluble in the first and second resin, the thinner and the solvents, and may be of the same or different colors or hues as well as chemical nature or composition, particle size, pH, and chromaticity. One of the advantages of a flocculated developer is that black developers, for example, may be produced from colored pigments chosen in proper proportion and having the proper relationship of individual colors to produce a black toner wherein all of the separate pigments are grouped together in substantially the same proportion within each association complex. This is to be contrasted to non-flocculated polychrome developers wherein each individual pigment particle is dispersed in the black developer and is movable as a separate and distinct entity as compared to the flocculated polychrome developers wherein each unit association complex, and marking element contains within itself the proper proportions of the several pigments necessary to provide the desired color or chromaticity, and which moves as a unit through the continuum or liquid vehicle of the developer during the deposition procedure.

Since according to the present invention all of the particles constituting the marking element of the desired color are grouped together in the desired proportion in each association complex, all of the particles in each complex are simultaneously deposited and there is substantially uniform depletion of toner pigments or pigment combination thereby maintaining good color control during use of the developer and during replenishment thereof with additional marking elements. In the case of a non-flocculated polychrome developer the situation is somewhat different since each particle of the developer is separately movable under the influence of the electrostatic field, resulting in a situation wherein there may be, and in fact often is, selective depletion of one type pigment or pigment combinations resulting in gradual changes of the color balance or chromaticity of the developer and the resultant image.

The marking element which includes the association complex and the envelope of the second resin carries a negative charge for attraction to and deposition on the surface as controlled by the electrostatic charges on that surface. Accordingly, the resolution of the resultant developed image is a function of the characteristics of the surface upon which the developer is to be deposited. Increased contrast including increased image coverage and reduction in background deposition, each of which is accomplished without substantial reduction in image resolution are possible in accordance with the present invention by providing a marking element having a controlled electrophoretic mobility and inertial stability. The former term relates to the ability of the marking element to move through the continuum or vehicle of the developer under the influence of an electrostatic charge, while the latter relates to the inertial response characteristics of the marking element in the presence of an electrostatic field.

With non-flocculated developers, imperfections in the imaging surface result in graininess in the image area and tinting or deposition in the non-image areas, since the fine size of the developer particles may be influenced by localized, residue electrostatic charges in the non-image areas, and do not possess sufficient inertia to resist attraction to these areas. In the case of the electrostatic field created by the image areas, the fine particles are attracted to the surface, but their deposition is also affected by the imperfections in the surface which may give rise to a grainy and discontinuous image lacking the desired contrast.

With the developer of the present invention wherein a multiplicity of marking particles are grouped together in the association complex, there is incraesed inertial stability due to increased size which is sufficient to resist movement due to the attractive forces of the electrostatic charges in the non-image areas, while the electrophoretic mobility of the particle is sufficient for attraction to the charges in the image area. Once deposited in the image areas the marking element includes a number of marking particles of relatively small size thus increasing image density by the simultaneous deposition of a number of particles, while substantially maintaining the resolution since the marking element is of relatively small size.

In a preferred form of the present invention, the liquid vehicle or continuum is removed after deposition of the marking element resulting in a sudden increase in the ratio of resin to thinner which brings about deflocculation and destruction of the oganosol, thus providing on the surface of the image member a multiplicity of marking particles which are adhered to the base by the first and second resins proviously used to form the association complex and the resin envelope, respectively. It is by this mechanism that fixing of the image is accomplished, and solidification of the resin may be by oxidation, reaction with the resin of the image surface, if one is present or adsorption into the surface.

Another object of the present invention is the provision of a liquid developer composition in the form of a paste which may be diluted with an electrically insulating liquid to provide a negatively charged organosol or emulsion type developer wherein each droplet thereof includes a first and second resin and a multiplicity of marking particles.

Another object of the present invention is the provision of a developer of the type described which includes an association complex of a first resin which is halogenated and a multiplicity of marking particles, and the association complex being surrounded by an envelope of a second liquid resin.

A further object of the present invention is the provision of an improved method of developing an electrostatic latent image with a liquid developer wherein relatively good resolution is achieved by utilizing negatively charged marking elements of relatively small size, wherein the marking particles may be fixed to the surface by removal of the liquid which constitutes the continuum or suspending medium therefor, and/or by heating to fuse the resin component of the developer.

A further object of the present invention is the provision of a toner paste which may be diluted to form a toner concentrate or developer useable in electrostatic photography wherein the toner paste includes a first and second liquid resin, and a multiplicity of marking particles, the first resin which is chlorinated upon dilution being capable of forming a flocculate in association with the marking particles, and the second liquid resin upon dilution being capable of forming an organosol wherein the second resin surrounds the association complex.

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

The developer of the present invention includes marking elements dispersed in a continuum or liquid vehicle which is electrically insulating in nature, and preferably, nonpolar, having a volume resisitivity in the order of 10^9 ohm/centimeter or higher, and which provides a suspend-

ing medium which will not discharge the electrostatic latent image during the development procedure, and which also provides the proper environment for the complex marking element of the present invention. The marking element itself includes two primary components, the first an association complex, and the second an envelope surrounding the association complex.

The association complex may be described as a stable association of primary particles held together by electrostatic or Van der Waal forces or bonds considerably weaker than primary chemical bonds. The association complex may have a regular geometric arrangement, for example body centered cubic, face centered cubic, laminal, or chains, and moves as a unit with the Browman movement of the primary particles effective mainly in causing the particles to relocate within the internal structure of the association complex. Forming a part of the association complex is a chlorinated first liquid resin characterized by its ability to flocculate in the presence of a thinner, or become non-compatible with the the inner at concentrations above a predetermined level wherein the resin within the thinner tends to agglomerate or precipitate out as resin particles or groups of resin particles. Ordinarily this characteristic of a resin is undesirable in liquid developers for electrostatic photography since it results in a non-stable developer wherein the developer phase settles out.

In accordance with the present invention this undesirable characteristic is controlled to provide a system wherein a stable flocculation size is achieved so that the marking particles, which form a part of the association complex can be drawn together by Van der Waal forces, or the other forces previously mentioned, into association with the flocculated resin phase. In this way, the association complex includes a multiplicity of marking particles held together by a sheath or network of a polymer around each marking particle.

As is understood, fine particles when suspended in a liquid exhibit a tendency to flocculate in accordance with the individual particle sizes, the smaller the particles the greater the tendency towards flocculation. In addition to the tendency of the marking particle to flocculate, there is also the deliberate and individual flocculation of the chlorinated first liquid resin so that in the presence of a multiplicity of marking particles and the first liquid resin, a flocculate is formed in the presence of a thinner above approximately a predetermined ratio which is a function primarily of the particular resin involved as well as the nature of the thinner.

It is thought that the mechanism to flocculate formation may proceed in two ways. In the first, the marking particle functions as a nucleation condensation center for the chlorinated liquid resin which is present in the mixture in relatively small amounts, for example, ranging from considerably less than to several times the amount of pigment and preferably about one part resin per part pigment. In this instance, the marking particles form an active site which attracts the resin molecules thereto so that the resin now preferably associates with the particles rather than being uniformly and evenly dispersed through the thinner.

In the second mechanism of flocculate formation, the resin is diluted in the thinner to a point wherein the individual molecules of the resin appear to behave as individual particles of relatively small size, and thus inherently tend to agglomerate at this dilute concentration. Similarly, the marking particles being of relatively small size inherently tend to flocculate. When resin and pigment are present in a thinner above the predetermined ratio, flocculation of both resin and pigment takes place again resulting in the formation of an association complex wherein the resin particles tend to center around the marking particles. In either case, the resultant structure or inclusion of resin provides a sheath or network of polymer around each marking particle.

Regardless of the mechanism of association complex formation, the group of pigment particles forming the complex are sufficiently stable to moderate stresses, such as fluid stresses, electrical stresses, and the like, to move as an integral unit, or as anentity when used in the developer. Subsequent to deposition on a surface and removal of the continuum, liquid thinner, vehicle or solvent, the predetermined relationship to thinner and resin and/or pigment no longer exists, and the flocculate or association complex may revert to a non-flocculated condition to form a relatively simple mixture or pigment dispersed in a resin in which the resin is grouped or centered around the pigment particles because of the fact that the pigment and resin are now deposited on a surface and physically maintained in close proximity to each other.

The second part of the marking element is a second liquid resin which forms an envelope around the association complex, this resin being characterized by its ability to form an organosol in the presence of a thinner above predetermined proportions of resin and thinner. Unlike the first resin, the second resin forms a droplet which is suspended in liquid, and this system may also be described as an emulsion wherein one liquid phase is uniformily dispersed in another liquid phase.

A desired effective average size of the association complex in suspension in the continuum is at least ten times larger than the intrinsic particle size of the marking particle, the intrinsic particle size of the pigment particels being less than approximately 5 microns and more than approximately 0.01 micron in the largest dimension. The first liquid resin upon dilution with a thinner to a ratio wherein flocculation occurs provides an intrinsic particle size in the largest dimension of the resin particle greater than 250 Angstrom units, and accordingly it is apparent that the resultant association complex and marking element may be relatively small in size thus providing good resolution with unexpectedly high contrast since a multiplicity of marking particles travel together during deposition because the association complex and marking element move as a unit.

Liquid paraffins, straight or branched chain, synthetic or distilled from petroleum and of low KB value have provided good results as carrier liquids. These materials promote developer stability in that they absorb a minimum amount of atmospheric water vapor while exhibiting a rapid evaporation rate which is a function primarily of the molecular weight so that the liquid may be removed within a relatively short period of time. If changes in KB value are indicated, it may be adjusted upward by adding, as needed, a relatively small quantity of liquid materials having a relatively high KB value, for example aromatics, olefins, ketones, esters and the like to provide a carrier having a KB value in the range of about 20 or 25 to 100.

It is preferred in accordance with the present invention that the carrier liquid be an odorless high molecular weight liquid paraffin which is relatively free of non-volatile residues which would tend to contaiminate the coating of the image bearing surface. Such contamination is detrimental to image quality particularly in those instances in which a series of images are to be developed seriatim on the same image bearing surface. This type liquid carrier is characterized by a clear, water white color, low odor, absence of sulfin compounds and olefins and generally having a boiling point in the range of 200° to 400° F.

Typical examples of other liquid materials which may be utilized include halogenated hydrocarbons ranging in molecular weight from about 137 to 205 and having a KB value ranging from about 25 to 70. Other materials which may be utilized include n-pentane, n-hexane, VM n-heptane, VM and P naphtha, high-flash VM and P naphtha, naphthanol mineral spirits, mineral spirits No. 10, Stoddard solvent, mineral spirits, high-flash mineral spirits, odorless mineral spirits, and kerosene, which exhibit a KB value in the preferred range of 25 to about 40.

Additional materials such as Isopar G and Isopar H, which are believed to be synthetic isoparaffins, and available from the Humble Oil and Refining Company in different boiling point ranges but essentially similar in KB values may also be utilized. These latter materials have a KB value of 27 to 28, an aniline point of between 180 and 185° F., and include C9, C10, C11 and C12 saturates in varying amounts. These materials have an average molecular weight of between 140 to 160.

The first resin may be a homopolymer of vinyl chloride or a copolymer of vinyl chloride and vinyl acetate, chlorinated rubber, chlorinated alkyd, or a chlorinated sucrose ester, or other halogen containing resin capable of flocculating in a thinner having a Kauri-butanol value of between about 20 to 125 and preferably in the range of 20 to 50. The vinyl chloride homopolymers preferably have a specific gravity of 1.3 to 1.45 and a specific viscosity in the range of 0.32 to 0.60. In the case of the vinyl chloride copolymers, the specific gravity may vary from 1.20 to 1.55 with a specific viscosity in the range of 0.15 to 0.40 and the inherent viscosity in the range 0.40 to 0.54 when tested by Method A of ASTM D–1243 with a cyclohexanone and 0.2 gram of resin per 100 milliliters. Also useable in accordance with the present invention are hydrolyzed copolymers of vinyl acetate and vinyl chloride.

In the case of the chlorinated rubber material, a preferred material in accordance with the present invention is a chlorinated polyisoprene contatining approximately 67% by weight chlorine although lesser percentages of chlorine may be utilized. The viscosity range in centipoises of the chlorinated isoprene may vary from 4 to 25.

The chlorinated alkyds in accordance with the present invention may vary from 10% to 50% chlorine by weight, and the alkyd may for example be a soya or linseed oil modified alkyd having between 50 and 65% oil content. In the case of chlorinated sucrose esters, a reaction product of a carbohydrate and a fatty acid are chlorinated to a percentage by weight of chlorine of between about 15% and 60%. The sucrose ester itself may be a diester or higher ester or coconut acid, cottonseed oil, acid tallow or fatty acids, hydrogenated tallow acids, lauric acids, myristic acids, palmitic, oleic, stearic, behenic, linoleic, linolenic, eleostearic and ricinoleic acids. The esters of the above mentioned acids with ethylene and propylene oxide adducts of carbohydrates, such as polyoxyethylene sorbitol, propyloxylpropylene sorbitol may be used as well as the fatty alcohols. Sucrose esters and diesters of varying degree of esterification ranging from 1 to 8 ester groups per molecule vary in hydrophilieliphile balance and other properties which indicate their degree of unsaturation, esterification, the range of fatty acid molecular weight, and the molecular weight distributions. These sucrose ester starting materials are chlorinated by dissolving them in carbon tetrachloride using an iodine catalyst and bubbling chlorine gas through the material for approximately one to four hours. The chlorination reaction is exothermic and therefore care should be taken during the chlorination procedure to prevent excess heat from being applied.

The halogenated resins and particularly those which are chlorinated are useful in the formation of negatively charged flocculated developers even with the use of carbon black pigments which vary from acid to basic in pH as measured in aqueous slurry. This characteristic in addition to the tendency of these materials to flocculate thus provides a group of resins which may be used as the first resin in a negatively charged multi-resin component liquid developer.

Satisfactory results may be achieved using a long, medium or sort oil alkyds, a bodied linseed oil or a rosin modified linseed oil or vinyl polymer or copolymer as the second resin. These resins are characterizezd by their ability to form an organosol at a predetermined ratio of thinner to resin, and preferably, the organosol is formed at a resin dilution which is somewhat higher than the resin dilution required to form the flocculate with the first resin.

The resin phase in accordance with the present invention essentially includes polymer molecules substantially soluble in a thinner at high polymer concentrations, the mixture containing molecules of polymer which differ in composition, structure or molecular architecture, or order of combination of monomer units so as to have variable solubility parameters which render the mixture capable of fractionation upon dilution with a solvent or thinner having electrical properties suitable for the process and compositions in accordance with the present invention. Upon dilution, polymer fractions will precipitate as a separate phase at progressive levels of dilution. The first components to separate upon solvent dilution with thinner have the capability of promoting coflocculation of the precipitated polymer with one or more types of imaging pigment particles. Subsequent dilution and precipitation of further fractions of polymer operate to deposit the further fractions of the polymer on the coflocculated, agglomerated resin particles, and causes particle growth by superficial accrual of deposited polymer on the original particles.

In general, the process of polymer precipitation following the primary nucleation in which the first polymer fraction associates with the pigment causes a continual growth of the primary coflocculates and a progressive depletion of residual or other fractions of polymer contained in the continuum or the thinner. A condition is finally achieved in which the system comprises a dispersion of particles having an internal viscosity substantially greater than that of surrounding continuum of thinner. The viscosity difference is sufficient to allow for the complex particle to be moved through the thinner continuum without disruption thereof by the shear stresses involved in its electrophoretic transport.

The polymer fraction last deposited, being more soluble than the earlier deposited polymer fractions, will be swollen by the solvent to a greater extent than the earlier deposited fractions. Hence, a viscosity gradient exists between the inner core of the association complex and the outer periphery of the marking element, which viscosity corresponds to the viscosity of the combined resin and thinner at various zones from the inner core outwardly to the outer periphery of the marking element, with the viscosity being substantially constant in the continuum. This reduces the sharpness of interphasal discontinuity so as to promote suspension stabilization. Slippage of the peripheral layer or layers of the marking element by laminar flow inhibits the influence of external turbulence which tends to disrupt the unitary structure of the element. Accordingly, even at high transport velocities, mixing of the constituents of the marking element is inhibited thereby maintaining integrity of the primary structure until it encounters the compaction forces present in the region of strongest electrical fields, for example, the fields associated with the image areas. In regions where electrical fields are weak, for example, discharged surface areas, the efficiency of attraction and deposition in these areas will be retarded because of the structural stability of the marking element.

The marking particle is preferably a solid which is insoluble in the thinner, solvent, first resin and second resin, and in accordance with the present invention, organic and inorganic colors and carbon blacks may be used. The organic colors include for example, Monastral Violet R, Red B, Green B, Blue BF, Phthalocyanine Zulu Green, Zulu Blue, Crotonfast Blue; Permanent Red, Green, Carmine Toner, Yellow Toner, Benzidine Yellow Toner, Transfast Yellow; Phospho-Tungstate Bluegrass Green and Nubian Resin Black. The inorganic pigments which operate satisfactorily include for example, pure black iron oxide, magnetic oxide, pure chromate, red oxide, pure red iron oxide, raw umber, burnt umber, the molyb-

date ming oranges, chrome yellows, lead chromate, chrominum green oxide, hydrated chromium green oxide, cobalt blue, solvent blue B, and iron blue. The carbon blacks which may be utilized include for example, the acetylene blacks, lamp black, gas furnace blacks, oil blacks, and channel blacks.

As is apparent, one or more of these pigments may be utilized in selected proportions to provide different colors, hues, reflection, and the like, as is well known in the art in mixing pigments. Likewise, various sizes of pigments may be used as pointed out in connection with the intrinsic particle size of the association complex.

In compounding the developers in accordance with the present invention, a paste may be formed, or a toner concentrate may be formed, either of which may be diluted to the proper solids content for use as a liquid developer. The paste is a somewhat viscous heterogeneous mixture of the first resin, the second resin, the marking particles, thinner, the thinner being present in an amount somewhat less than that required to form the flocculate or the organosol, but present in an amount sufficient to provide a grinding consistency. The toner concentrate on the other hand includes the marking elements, or the coordinated association complex and resin envelope, with the marking elements having a negative charge as previously described. Generally, the solid contents of the toner concentrate is in the range of about 3% to 35%, with the preferred range of about 10% to 25%. Although this represents a solids content somewhat higher than that customarily used in developing an electrostatic latent image, the toner concentrate may be used as a developer in which case the marking elements deposited on the non-image areas by a mechanical action rather than an electrostatic attraction may be substantially removed by washing or rinsing the image surface with an electrically insulating liquid. The toner concentrate when diluted to a solids content of between about 0.25% to about 3% may be used directly as a developer. In the case of the toner concentrate, dilution is accomplished by adding the concentrate to the electrically insulating liquid thus inherently allowing the use of a system wherein proper developer concentration may be achieved by adding toner concentrate to the liquid developer already being utilized in the system. In the case of the paste, it is generally required that liquid thinner be added to the paste rather than vice versa, and this offers the advantage of being able to provide a paste which may be diluted down to the proper solids content as required either for the toner concentrate or the liquid developer.

Compounding of the various components of the developer system may be accomplished on a three-roll mill, or other equivalent apparatus in which the resin, or combinations thereof, and marking particles are mixed with a sufficient amount of thinner, as previously described, to provide a workable consistency for grinding the marking particles into the resin and to bring about reduction in marking particle size, if required.

By this procedure a viscous toner paste is formed in which the mixture may include a sufficient amount of solvent to enable mechanical working, and the amount of this solvent is somewhat less than that required to bring about flocculation of the first resin or formation of the organosol as provided in the second resin. Since the first resin tends to flocculate in the presence of thinner in a first predetermined amount, and the organosol tends to form in the presence of a second predetermined amount of thinner which is greater than the first, the paste can be diluted with a liquid carrier which includes a sufficient amount of thinner to bring about first flocculation and secondly the organosol formation, as may be physically measured by the sudden change in viscosity of the mixture from a viscosity close to that of the paste to a viscosity close to that of the liquid continuum or suspending medium. As previously stated, the toner concentrate, may include only a sufficient amount of thinner to provide flocculation or agglomeration with the balance of the suspending medium to be added later to establish the dilution which forms a developer, the electrically insulating liquid being added to form the developer having a Kauri-butanol value equal or less than that of the solvent in the concentrate.

In the case of preparation of the composition in accardance with the present invention by a ball mill or paint shaker using steel balls, the pigment is preferably dispersed in a sufficient amount of chlorinated resin to exceed the resin or oil absorption end-point. This amount may be determined by titrating the pigment with resin and blending the combination until a sufficient amount of resin is added to wet out the pigment completely.

The pigment and resin dispersion may be performed on a paint conditioner or shaker with the dry pigment and chlorinated resin being placed in a suitable container with steel balls present in such a quantity that the pigment-resin charge slightly more than fills the voids between the steel balls. The viscosity of the mixture is adjusted by adding thinner in an amount consistent with steel ball mobility and proper cascading of the charge in the container. The optimum grinding or dispersion is obtained when the balls do not "lock up." Initial grinding time varies with the container size, size and number of balls, density, bulking value and oil absorption characteristics of the pigment. During this operation, other additives may be added, as desired, to improve the characteristics of the ultimate developer.

By the above precedure, the various components are added in a sequence which promotes or facilitates the formation of the flocculate and the organosol, with care being taken during the compounding procedure to avoid any sequence which detracts or interferes with the formation of the association complex of organosol.

The following specific examples illustrate preferred embodiments of the present invention:

EXAMPLE 1

50 grams of an oil black having a pH in the range of 7 to 8.5 were dispersed in 150 grams (34% solids) of a vinyl acetate-vinyl chloride copolymer in Cellosolve acetate and 240 grams (70% solids) of a soya modified alkyd containing 65% soya oil and approximately 24% phthalic anhydride, the alkyd having an acid number of 8 and being dispersed in mineral thinner. Cellosolve acetate contains about 95% ester, has a flash point of 120° F. (open cup) and has a specific gravity of between 0.971 and 0.976. This mixture was processed on a three-roll mill to disperse the pigment. 42 grams of this dispersion were mixed with an additional 53 grams (70% solids) of the alkyd resin and diluted with Isopar G, the synthetic isoparaffinic material previously described, to provide a negatively charged toner concentrate.

EXAMPLE 2

6 grams of the pigment of Example 1, 3 grams of the vinyl acetate-vinyl chloride copolymer of Example 1, and 170 grams (70% solids) of the alkyd resin of Example 1 were processed and diluted with Isopar G to provide a negatively charged toner concentrate.

EXAMPLE 3

6 grams of a 20% solids solution of a hydrolyzed vinyl acetate-vinyl chloride copolymer in xylol were mixed with 6 grams of the pigment set forth in Example 1 and 170 grams (70% solids) of the alkyd resin of Example 1. This dispersion was diluted with Isopar G to provide a negatively charged toner concentrate.

EXAMPLE 4

12 grams of a 10% solids solution of a hydrolyzed vinyl acetate-vinyl chloride copolymer in xylol were treated on a three-roll mill with 6 grams of the pigment of Example 1 and 24 grams (70% solids) of the alkyd resin of Example 1. Thereafter an additional 146 grams (70% solids) of the alkyd resin was added and the mixture diluted

with Isopar G to provide a negatively charged toner concentrate.

EXAMPLE 5

1.8 grams of Pyrazell Red Toner (pyrazolene) having a pH of about 6 to 7, 2.4 grams of phthalocyanine blue having a pH of between 5 and 6 and 1.8 grams Permanent Green pigment having a pH of between 6 and 7 were mixed with 1.2 grams of a 20% solution of a hydrolyzed vinyl acetate-vinyl chloride copolymer in xylol. To this was added 24 grams (70% solids) of an alkyd resin as per Example 1 and the mixture was processed on a three-roll mill to disperse the pigment. Thereafter an additional 146 grams (70% solids) of the alkyd resin was added and the material blended to disperse the additional alkyd and diluted to one pint with Isopar G to provide a negatively charged toner concentrate.

EXAMPLE 6

12 grams of 10% solution of hydrolyzed vinyl acetate-vinyl chloride copolymer in Cellosolve acetate and 3 grams of an epoxidized oil plasticizer in Cellosolve acetate, 24 grams (70% solids) of the alkyd resin of Example 1 and 6 grams of a channel black having a pH of between 2 and 4 were processed on a three-roll mill to disperse the pigment. After dispersion, an additional 144 grams (70% solids) of the alkyd were added and the material blended to disperse the additional alkyd. Thereafter the dispersion was diluted to one quart with Isopar G to provide a negatively charged toner concentrate.

EXAMPLE 7

6 grams of a 25% solution of vinyl acetate-vinyl chloride copolymer in Cellosolve acetate, 3 grams of an epoxidized oil plasticizer, 12 grams (70% solids) of the alkyd of Example 1, 3 grams of the channel black of Example 6 and 1 gram of the blue pigment of Example 5 were processed on a three-roll mill to disperse the pigment. After dispersion an additional 80 grams (10% solids) of the alkyd were added and the mixture diluted to which one pint with Isopar G to provide a negatively charged toner concentrate.

EXAMPLE 8

12 grams of a 10% solution of a hydrolyzed vinyl acetate-vinyl chloride copolymer in Cellosolve acetate, 2.4 grams of blue pigment, 1.8 grams of green and 1.8 grams of red and 1.5 grams of black pigment, all of Example 1, and 40 grams (70% solids) of the alkyd resin of Example 1 were processed on a three-roll mill to disperse the pigment. After dispersion an additional 106 ample 1, and 40 grams (70% solids) of the alkyd resin grams (70% solids) of the alkyd were added and the mixture diluted to one pint to provide a negatively charged toner concentrate.

EXAMPLE 9

12 grams of a 10% solution of a hydrolyzed vinyl acetate-vinyl chloride copolymer in Cellosolve acetate, 1.2 grams of the blue, .9 gram of the red, .9 gram of the green pigments of Example 5, 3 grams of the black pigment of Example 5, and 5 grams of epoxidized oil plasticizer and 40 grams (70% solids) of the alkyd resin of Example 1 were processed on a three-roll mill to disperse the pigment. After dispersion an additional 106 grams (70% solids) of the alkyd were added and the mixture diluted to one pint with Isopar G to provide a negatively charged toner concentrate.

EXAMPLE 10

14 grams (70% solids) of the alkyd resins of Example 1, 13 grams of chlorinated rubber (viscosity of 6 centipoises) in 18 milliliters toluol, 3 grams of the oil black pigment of Example 1 were processed on a three-roll mill to disperse the pigment. After dispersion an additional 67 grams (70% solids) of the alkyd were added and the mixture was diluted to one pint with Isopar G to provide a negatively charged toner concentrate.

EXAMPLE 11

14 grams (70% solids) of the alkyd of Example 10, 15 grams of chlorinated rubber (viscosity of 20 centipoises) in 18 milliliters of toluol, 2.4 grams dibutyl phthalate plasticizer, and 3 grams of the oil black pigment of Example 1 were processed on a three-roll mill to disperse the pigment. After dispersion an additional 67 grams (70% solids) of the alkyd were added in addition to 17 milliliters of toluol and mixed to disperse the additional alkyd resin. The dispersion was diluted with Isopar G to provide one-half pint of negatively charged toner concentrate.

EXAMPLE 12

20 milliliters of linseed oil and 13 grams of chlorinated rubber (viscosity of 5 centipoises) were heated together at 220° F. for fifteen minutes to dissolve the rubber. Thereafter 14 grams (70% solids) of the alkyd of Example 1 and 4 grams of oil black were added and dispersed. After dispersion an additional 40 grams (70% solids) of the alkyd was added and the material was allowed to cool followed by dilution of Isopar G to form one pint of negatively charged toner concentrate.

EXAMPLE 13

3 grams of oil black of Example 1, 12 grams (25% solids) of a chlorinated surcrose ester in carbon tetrachloride, and 86 grams (70% solids) of the alkyd resin of Example 1 were processed on a three-roll mill to disperse the pigment and thereafter diluted with Isopar G to provide a negatively charged toner concentrate.

EXAMPLE 14

The procedure set forth in Example 13 was followed except that 12 grams (25% solids) of a chlorinated alkyd which was a medium oil linseed alkyd having an acid number of 5 to 10 and an oil content of about 55% was dissolved in carbon tetrachloride and substituted in place of the chlorinated sucrose ester and processed as described in Example 13 to provide a negatively charged toner concentrate.

EXAMPLE 15

3 grams of the pigment of Example 1, 6 grams (50% solids) of chlorinated rubber (viscosity of 5 centipoises) in Celloslove acetate, 20 grams (70% solids) of the alkyd of Example 1 were processed on a three-roll mill to disperse the pigment. After processing, an additional 61 grams (70% solids) of the alkyd were added and the dispersion diluted to one pint with Isopar G to provide a negatively charged toner concentrate. When diluted to developer concentration and used to develop an image, this material was heat fixed to increase the smudge resistance by fusing the resin components of the developer.

EXAMPLE 16

3 grams of the carbon black pigment of Example 1, 18 grams (40% solids) of a chlorinated alkyd in xylene, the alkyd resin being a soya modified alkyd having an oil content of 65% and a phthalic anhydride content of 24%, and 20 grams (70% solids) of the alkyd of Example 1 were processed to disperse the pigment and 66 grams (70% solids) of additional alkyd resin were added and blended to disperse the components. Thereafter the dispersion was diluted to one pint to provide a negatively charged toner concentrate.

EXAMPLE 17

3 grams of the carbon black pigment of Example 1, 20 grams (70% solids) of the alkyd of Example 1, and 9 grams of a 40% solids solution of chlorinated sucrose tetralinoleate in xylene were processed on a three-roll mill to disperse the pigment. After processing an additional

66 grams (70% solids) alkyd were added and the material was diluted to one pint with Isopar G to provide a negatively charged toner concentrate.

The above examples also show that plasticizers and stabilizers may be used for the resin phase if needed, and the materials specifically set forth therein are merely illustrative of several types of materials which may be added and which exhibit no adverse affect on the developer. It is also to be noted in the above examples that in some instances the resin materials were dispersed in liquids other than the thinner, for example, xylol, toluol, Cellosolve acetate and linseed oil.

Dilution of the toner concentrate as set forth in Examples 1 to 17 provides a liquid developer wherein the marking elements thereof carry a negative charge for attraction to and deposition on the surface of an image bearing member in conformity to the charge pattern thereon. The image bearing surface may be paper to which a charge pattern has been transferred, or an electrically insulating photoconductive surface including zinc oxide or other finely divided photoconductor dispersed in a film forming binder. The film forming binder is preferably a polymer including polar functional groups thereon, and thus stable in the non-polar liquid medium of the present invention.

Development is accomplished by immersing, flowing, applying with a roller or treating the surface of the image bearing member so as to bring the liquid developer into close proximity to the electrostatic image. Due to the electrostatic attraction between the image and the marking elements, the marking elements migrate towards the surface and deposit thereon a pattern as controlled by the electrostatic latent image. Upon removal of the liquid continuum, in the preferred form of developer, as by use of a squeegee roller, or the combination of a squeegee roller and heat, the amount of thinner is reduced below that needed to provide flocculation and organosol formation to allow the marking element to deflocculate or revert to a mixture of resins and pigment particles. The resin may be fixed by oxidation, or through the use of driers which accelerate or promote oxidation, or by reaction with a component or components of the base upon which it is deposited such as by cross-linking between the resin or resins of the developer and the film forming binder, or by heating to fuse the resin phase. If desired, a counterelectrode unit may be utilized to enhance development as is well known in the art.

In the case of developers using a magnetic material such as magnetic iron oxide, the developer may be applied under the influence of a magnetic field. This is done from a liquid medium and offers the advantage of maintaining substantially dielectric conditions during development. In this instance, the association complex constitutes a group of magnetic particles and a first resin, and the total electrophoretic mobility associated with marking element deposition as controlled by the electrostatic latent image exceeds the influence of the magnetic field upon the complex. In this way deposition in the image areas is controlled by the electrostatic image while deposition in the non-image areas is substantially eliminated because of the influence of the magnetic field.

While the present invention has been described with reference to electrophotography, it is to be understood that the principles thereof are equally applicable to developers and methods of developing electrostatic images on an electrically insulating surface which have been formed by other means well known in the art. Accordingly, the present invention has been described with reference to specific methods, as well as preferred embodiments thereof, and it is not intended that such details be regarded as limitations upon the scope of the invention except so far as included in the accompanying claims.

What is claimed is:

1. A liquid developer composition for developing an electrostatic latent image on the surface of an image bearing member for rendering a latent electrostatic image visible and for providing a fixed visible image on said surface, where the developer consists essentially of an electrically insulating liquid having a Kauri-butanol value of between 20 and 100 and having dispersed therein a plurality of marking elements each having an electrostatic charge for deposition on said surface as controlled by the electrostatic charges thereon, and wherein each marking element includes a plurality of different resins and a plurality of pigment particles for imparting visible color thereto, said resins operative as a fixing agent to adhere said pigment particles to said surface upon removal of a substantial portion of said electrically insulating liquid, said plurality of resins consisting essentially of a first liquid resin insoluble in said insulating liquid and selected from the group consisting of homopolymers of vinyl chloride, copolymers of vinyl chloride and vinyl acetate, chlorinated rubber, and chlorinated sucrose esters and a second liquid resin which is non-halogenated and different from said first resin and insoluble in said electrically insulating liquid selected from the group consisting of short, medium and long oil alkyd resins, bodied linseed oil, rosin modified linseed oil, and vinyl polymers and copolymers, said first resin being present in an amount between $\frac{1}{3}$ and $\frac{1}{480}$ of the weight of said second resin, said first and second resin being present in an aggregate amount by weight greater than the weight of said pigment particles, said pigment particles being present in an amount by weight of between 0.2 and twenty four times the weight of said first resin, and the total solids content of said developer being 35% by weight or less.

2. A liquid developer as set forth in claim 1 wherein said solids content is 3% by weight or less.

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U.S. Cl. X.R.

117—37; 252—308; 260—33.6, 33.8

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,507,794 Dated April 21, 1970

Inventor(s) Donald L. Fauser and Edward G. Bobalek

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 4, line 1, "residue" should read --residual; line 11, "incraesed" should read --increased--; line 30, "proviously" should read --previously--.

Column 5, line 20, "the the inner" should read --the thinner--; line 49, "to" should read --of--.

Column 6, line 4, "anentity" should read --an entity--.

Column 7, line 21, cancel "in the range" and insert --may vary from--.

Column 11, cancel beginning with line 51 through line 54 and insert the following: --grams (70% solids) of the alkyd were added and the mixture diluted to one pint to provide a negatively charged toner concentrate.--.

Column 13, line 29, following "electrostatic" insert --latent--; line 32, following "thereon" insert --in--.

Column 14, line 8, following "specific" insert --examples and--.

SIGNED AND SEALED

SEP 29 1970

(SEAL)
Attest:

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