

1

3,391,014

LIQUID DEVELOPMENT OF ELECTROSTATIC IMAGES

Donald L. Fauser, Cleveland, Ohio, assignor to Harris-Intertype Corporation, Cleveland, Ohio, a corporation of Ohio

No Drawing. Filed Apr. 27, 1964, Ser. No. 362,961

4 Claims. (Cl. 117—37)

ABSTRACT OF THE DISCLOSURE

Polychrome developers for electrostatic photography include at least two groups of pigments whose pH are relatively close in order to provide developer particles of essentially the same electrophoretic mobility through an electrically insulating liquid. Above a pH of 6.4, a positive developer is provided while below the pH of 6.4 a negative developer is provided. The developer also includes a resin which, with the pigment, forms a two phase system. By maintaining the pH of the pigments fairly close together, the pigments deposit in the proper ratio to maintain the preselected color balance.

This invention relates to electrostatic printing and more particularly to an improved liquid developer, the method of making such a developer, and the method of using such a developer to develop an electrostatic latent image.

Recently, developer systems have been proposed which make it possible to develop images with improved clarity, contrast and definition. One such system is disclosed in the Metcalfe et al. article on "Liquid Developers for Xerography," the Journal of Scientific Instruments, vol. 32, February 1955, pages 74 and 75. The developer disclosed in this article represents a relatively simple system including a dispersion of finely divided carbon black in an electrically insulating liquid. Such a developer may be employed with photoconductive plates, drums or papers, and it may be necessary to employ a separate fixing operation in order to achieve the desired permanency of the developed image.

Another type of liquid developer is disclosed in the United States patent to Metcalfe et al. 2,907,674 issued Oct. 6, 1959 in which a control agent is added to the developer mixture to modify the charge on the pigment and wherein the control agent is described as acting as a fixing agent. The Metcalfe et al. patent utilizes a relatively small percentage of resin or fixing agent in proportion to the amount of pigment present in the developer composition. It is also stated in the Metcalfe et al. patent that an alkyd resin provides a positively charged developer while a linseed oil resin provides a negatively charged developer.

One of the disadvantages of the liquid developer systems previously described has been the tendency of the developer particles to flocculate or agglomerate and settle out in the liquid carrier so that the developer composition as a whole is no longer suitable for use in developing an electrostatic image. Another difficulty which has been encountered is non-uniform polarity, gradual shift or change in the polarity of the developer or a tendency to reverse polarity upon standing or during use.

Liquid developers generally provide the advantage of fine particle size as compared to dry powder developers, and better resolution is achieved with liquid developer systems. However, there exists a tendency for the fine pigment particles in a liquid developer to flocculate or to agglomerate in the absence of a stabilizing material. As a general rule, the finer the pigment particle size the more the pigment in the system exhibits a tendency to flocculate or agglomerate thereby reducing the relatively high

2

resolution which is potentially possible with liquid developers.

Accordingly, it is a primary object of the present invention to provide a liquid developer which possesses a stable polarity and which is substantially self-fixing upon removal of a substantial amount of the carrier liquid following deposition of the developer particles.

Another object is to provide a liquid developer composition which has relatively finely divided pigment or mixtures of pigment dispersed therein and wherein the pigment is easily dispersed and relatively non-settling.

Another object of the present invention is to provide a liquid developer composition which includes finely divided water insoluble organic pigments or mixtures of such pigments dispersed therein and wherein provision is made to render the dispersion relatively stable.

A further object of the present invention is to provide a liquid developer wherein the marking particle includes an organic water insoluble pigment, or mixture of such pigments, and wherein provision is made to render the marking particle substantially self-fixing upon removal of a substantial amount of the carrier from the image surface.

A further object of the present invention is to provide a liquid developer having dispersed therein marking particles of different color wherein all of the marking particles possess substantially the same polarity and mobility characteristic in the carrier, and wherein the marking particles are substantially self-fixing upon removal of a substantial portion of the carrier following deposition on an image bearing surface.

A further object of the present invention is the provision of an improved method of developing an electrostatic latent image by an improved developer composition.

A further object of the present invention is the provision of a method of compounding a developer composition for electrostatic photography.

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

The liquid developer of the present invention includes a marking particle which is dispersed in an electrically insulating liquid, and the marking particle preferably includes a pigment component which may be a pigment particle or aggregate, or a mixture of pigments and a resin, the latter forming an encapsulating envelope surrounding the pigment component. The developer is a two-phase system including a carrier which is an electrically insulating liquid and a colloiddally dispersed or emulsified phase which is the marking particle.

The pigment or mixture of pigments included in the marking particles are preferably finely divided organic materials or ionic, crystalline inorganic materials and the resin which also forms part of the marking particle operates to wet the pigment and to form an emulsion including the pigment or mixtures thereof and to bind the marking particle to the image bearing surface upon removal of the electrically insulating carrier liquid.

The electrically insulating liquid is preferably a non-polar liquid having a volume resistivity sufficiently high to prevent discharge of the electrostatic latent image, for example about 10^9 ohm-centimeters, or higher. The liquid is characterized by a Kauri-Butanol value, or solvency power, sufficiently low to permit formation of two phases in the presence of the resins in accordance with the present invention, but not so low as to collapse the gelatinous resin envelope thereby destroying the stability of the emulsion or dispersion and not so high as to dissolve the resin envelope.

Liquid paraffins, straight or branched chain, synthetic or distilled from petroleum and of low K-B 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 K-B value are indicated, it may be adjusted upward by adding, as needed, a relatively small quantity of liquid materials having a relatively high K-B value, for example aromatics, olefins, ketones, esters and the like to provide a carrier having a K-B 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 contaminate 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 serially on the same image bearing surface. This type liquid carrier is characterized by a clear, water white color, low odor, absence of sulfon 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 K-B 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, Varsol-1, Varsol-2, high-flash mineral spirits, odorless mineral spirits, and kerosene, which exhibit a K-B 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 K-B values may also be utilized.

The pigment in accordance with the present invention may be selected from any in the following table:

PIGMENTS		
	Supplier	pH
INORGANIC		
Pure Black Iron Oxide BK-250.....	C. K. Williams Co.....	9.49
Pure Black Iron Oxide BK-247.....	do.....	9.46
Magnetic Oxide IRN-351.....	do.....	7.64
(Mineral) Mango Violet 4813.....	Harshaw Chemical Co.....	4.08
Pure Kroma Red Oxide RO-3097.....	C. K. Williams Co.....	6.15
Pure Red Iron Oxide R-8098.....	do.....	6.77
Pure Red Iron Oxide R-2899.....	do.....	5.08
(Molybdate) Ming Orange, Dark 2527.....	Harshaw Chemical Co.....	5.33
(Molybdate) Ming Orange, Med. 2525.....	do.....	5.34
(Molybdate) Ming Orange, Lt. Ink 2502.....	do.....	4.97
C.P. Chrome Yellow, Primrose-Ink 2700.....	do.....	6.62
C.P. Chrome Yellow, Med.-enamel 2343.....	do.....	4.79
C.P. Chrome Yellow, Light-Ink 2701.....	do.....	4.63
Cobalt Blue (Aluminate) PX 922.....	do.....	9.93
Solvent Blue B (Zinsser) D1627.....	do.....	9.45
C.P. Iron Blue-Toning-Ink 4207.....	do.....	9.48
C.P. Iron Blue Softex-Enamel 4200.....	do.....	4.09
C.P. Iron Blue Melori-Ink 4055.....	do.....	3.88
C.P. Iron Blue Melori-Ink 4056.....	do.....	3.77
ORGANIC		
Monastral Violet R RT-791-D.....	E.I. duPont de Nemours & Co.....	9.29
Monastral Red B RT-790-D.....	do.....	8.78
Permanent Red-2B, Citation, Lt. (Ba) 1058.....	Harshaw Chemical Co.....	9.84
Permanent Red-2B, Citation, Med. Yel. 1059.....	do.....	8.32
Permanent Red-2B, Citation, Toner 1053.....	do.....	8.52
Permanent Carmine Toner ID-8710.....	do.....	6.45
Pyrazell Red Toner (pyrazolone) 1D-1970.....	do.....	6.23
Bontone Brown Y 7D-2250.....	do.....	7.55
Yellow Toner 3D-1840.....	do.....	6.78
Benzidine Yellow Toner 3D-2052.....	do.....	6.85
Benzidine Transfast Yellow 1275.....	do.....	6.81
Sunset Gold Toner 3D-8820.....	do.....	5.72
Green gold, YT-562-D.....	E.I. duPont de Nemours & Co.....	8.23

PIGMENTS—Continued

	Supplier	pH
Monastral Green B GT-674-D.....	do.....	8.08
Pigment Green B 3890.....	Harshaw Chemical Co.....	6.67
Permanent Green 300 3D-8322.....	do.....	6.56
Phthalocyanine-Zulu Green, 3826.....	do.....	6.10
Phospho-Tungstate Bluegrass Green 3910.....	do.....	4.48
Monastral Blue BF BT-425-D.....	E.I. duPont de Nemours & Co.....	7.88
Phthalocyanine-Zulu Blue Toner 4852.....	Harshaw Chemical Co.....	8.34
Phthalocyanine-Zulu Blue 4860.....	do.....	6.57
Phthalocyanine-Zulu Blue, Flocc. resist 4863.....	do.....	5.37
Phthalocyanine-Crononfast Blue 5D-4350 NCNF Toner.....	do.....	4.54
Black Pigment No. 90, Master Standard.....	do.....	6.58
Black No. 12082.....	Dimlich-Radcliffe-Colliway Color Company.....	9.41

We have found that the polarity of the developer, particularly in the case of inorganic crystalline materials appears generally to be related to the pH of the pigment as measured in deionized water and in the case of the organic materials, the polarity of the developer is closely correlated to the pH of the pigment determined in aqueous suspension. The results indicate that in general all commercially available pigments have a measurable pH which can be correlated to developer polarity, and in the case of the organic pigments, those having a pH greater than about 6.4 in an aqueous suspension provide a positive developer and those having a pH less than about 6.4 provide a negative developer when used with the binders and carrier liquids in accordance with the present invention.

The intrinsic particle size of the pigment particles is preferably approximately less than 5 microns and more than 0.01 micron in the largest dimension thereby providing a marking particle which is substantially smaller than particle sizes of the conventional developers and sufficiently small to provide resolution of 50 to 180 lines per millimeter. Preferably, the pigment component is made up of finely divided solid particles having a surface capable of adsorbing materials having a specific affinity for the surface and being characterized by a surface area, as measured by electron microscopy or nitrogen adsorption, of approximately five to several hundred square meters per gram. As is apparent, one or more of these pigments may be utilized in selected proportions in the developer to provide different colors, hues, reflection and the like.

The resins usable to form the dispersed phase in accordance with the present invention are preferably liquid and are characterized by a decreasing solubility with increasing concentration of carrier liquid of the type previously described, and their ability to provide an organosol, emulsion or stable suspension of non-flocculating colloidal particles when in the presence of a carrier liquid. The resin is compatible with the carrier liquid up to a predetermined relative proportion of carrier liquid to resin wherein the viscosity of the mixture is relatively high as compared to the viscosity of the carrier. Above the predetermined relative proportion of carrier liquid to resin, the resin and carrier liquid are not compatible and form a stable two phase system including dispersed particles of resin rather than a sedimentary precipitate, and the viscosity of the two phase stable dispersion of resin in carrier is essentially the viscosity of the carrier. These resins are characterized by their ability to form a particulate colloidal dispersion, stable emulsion, organosol or suspension when diluted to between 4 and 800 times their weight with a carrier liquid having a K-B value of between about 20 and 70.

The resin is preferably a viscous liquid at a temperature less than 150° C. but may be a solid and dissolved in a relatively small amount of solvent to provide a liquid resin mixture. A suitable solvent may be for example a non-polar solvent or thinner of relatively low K-B value,

and the resin and solvent are so coordinated and correlated that the solvent will not subsequently function as a contaminant and the combined characteristics of the resin and solvent are such that they are capable of forming an organosol when diluted with a carrier liquid of the above type to a concentration wherein a substantial fraction of the resin is incompletely soluble as a molecular dispersion in the carrier liquid. The resins which may be used in accordance with the present invention are preferably alkyd resins, or condensation or esterification products of one or more saturated or unsaturated polycarboxylic acids and one or more polyhydric alcohols. Such resins may be modified with one or more mono carboxylic acids such as drying or non-drying vegetable oil acids, and their solubility may be influenced by the extent of condensation which controls the average molecular weight and the molecular weight distribution of the alkyd polymer. These particular materials appear advantageous because they produce clear, hard, fast drying films resistant to aqueous solutions and hydrocarbon solvents. The latter characteristic is of significance particularly wherein an image bearing member having a developed image thereon is to be treated to form a second image thereon.

The ability of the alkyds to dry in air depends upon the oil length of the alkyd and the nature of the oil modification thereof. Drying oils containing unsaturated linkages combine with oxygen from the atmosphere to form a reaction product that polymerizes the modifying oils to form a continuous carrier liquid insoluble film. Accordingly, one feature of the present invention is the fact that the resin component may be caused to fix to an imaging surface by removing the surrounding carrier liquid thereby providing access to atmospheric oxygen for polymerization as previously noted. Generally, alkyd resins are classified according to the relative amount of oil used with respect to the phthalic anhydride, and the short oil alkyds generally contain 25 to 45% oil, the medium oil alkyds 45 to 65% oil and the long oil alkyds between 65 and 85% oil.

As the oil length decreases, acid value, viscosity, molecular complexity and cross-linking increase while solubility in high boiling petroleum and aliphatic solvents decrease. In accordance with the present invention the medium and long oil alkyd resins are preferred since they appear to be superior in maintaining charge polarity while providing hard and scuff resistant films.

Alkyds which may be used for example include resins made up of 60 to 70 parts mixed linoleic and linolenic fatty acids and about 30 to 35 parts of approximately equivalent molecular proportions of pentaerythritol and phthalic anhydride. Also, alkyds of about 55 to 65% mixed linseed oil fatty acids reacted with glycerol and phthalic anhydride in molecular ratios of 1.05 to 1.15 molecules of glycerol per molecule of phthalic anhydride are useful. An alkyd prepared so as to be a hydrocarbon soluble resin of acid value of less than 15 and viscosity less than E at 40% non-volatile content wherein the viscosity is rated in the Gardner-Holt scale at 77° F. has also been found to be satisfactory.

In addition, oleo resin varnish which is comprised of rosin modified phenolic resin and mixed linseed and tung oil in such proportions as to provide 70 to 80 gallons of mixed oil per 100 gallons of varnish operate satisfactorily. This particular material is heat blended and bodied at a temperature 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 K-B value equal to 35, the viscosity having been measured on a Gardner-Holt scale at 77° F.

The alkyds which have been successfully used may be modified with linseed oil, castor oil, soya oil, dehydroxylated castor oil, coconut oil, cotton seed oil, otiticia, palmitic oil, peanut oil, safflower, tall oil or mixtures thereof. These alkyds may be modified to provide the

desired oil content, and other properties as heretofore noted.

The alkyd to be used may be a long, medium or short oil alkyd wherein the proportion of oil is coordinated and correlated with the K-B value of the carrier liquid to provide a resin which is capable of forming an organosol at a dilution level wherein the resin becomes substantially insoluble in the carrier liquid. In addition, fractions of such alkyds may exhibit an intrinsic viscosity as measured in substantially anhydrous keton solvents which varies between 1.0 and 0.01 indicating a molecular weight range between 2,000 and as high as 100,000. These resins are also characterized by an acid value between 3 and 50, and it is preferred that the acid value be between about 3 and 10.

In addition to the resins previously mentioned, oleo resinous vinyl polymers and copolymers, and modifications thereof may be utilized. For example, the reaction product of the vinyl alcohol and long chain fatty acids or mixtures thereof such as myristic, palmitic, oleic, stearic, behenic and ricinoleic acid and the like is prepared by condensation and thereafter polymerized through the double bonds of the vinyl or ethylenically unsaturated portion of the resultant reaction product previously associated with the vinyl alcohol.

In formulating the developer in accordance with the present invention, the first step includes dispersing a predetermined amount of pigment in enough liquid resin or binder to exceed the binder or oil absorption end point. The amount of binder to be used may be determined by titrating the pigment with the binder and blending the two together until sufficient binder has been added to wet out the pigment completely, and the predetermined amount of binder may vary with each different type pigment. The mixture of binder and pigment may be processed on a ball mill or three roll mill or other suitable pigment grinding equipment. The viscosity may be adjusted by the addition of carrier liquid to provide a mixture having a consistency suitable for processing in accordance with the particular apparatus being employed. At this point, other additives may be incorporated into the mixture to improve pigment dispersion or to promote organosol formation or to facilitate the chemical reaction by which the binder becomes fixed to the surface upon which it is deposited. For example surfactants or driers such as metal salts of fatty acids and the like may be added in small percentages. The ratio of pigment to binder solids at the oil absorption end point is approximately 1 to 2.5 or less. This ratio and ratios as small as 1 to 70 may be utilized in the developers of this invention with the preferred ratio being approximately 1 to 14 to 1 to 20. The resultant material is a paste containing 55 to 60% solids with the continuous homogeneous phase or solution including the binder and the carrier containing the dispersed pigment. In this form, the binder acts as a solvent for the carrier, and the viscosity of the liquid resin or binder carrier solution is relatively high and is characteristic of the viscosity of the binder itself.

In cases where the resin is present in large amounts in proportion to the pigment, the optical density of the image due to pigment deposition is somewhat less than that desired, while with too little resin, an envelope may not be formed, or the developed image may exhibit less smudge resistance and poor squeegee characteristics, and the developer may exhibit a tendency to flocculate or settle out and agglomerate.

The toner paste is thereafter reduced in solids content to approximately 25% by addition of aliquots of carrier liquid until the phase inversion takes place at which point the carrier becomes the continuous phase and the resin becomes the dispersed phase resulting in the two-phase organosol or emulsion type system in which the pigment is entrained or carried by the dispersed phase. At this point, the toner concentrate has a relatively low

viscosity which is essentially the viscosity of the carrier. Although the percentage of solid materials in the concentrate is somewhat higher than that customarily used during development, each portion of the dispersed phase or each dispersed marking particle carries a characteristic charge which is primarily a function of the pH of the pigment as determined from pH measurements taken in distilled water as previously noted.

To provide a preferred composition suitable for development of an electrostatic latent image, the toner concentrate is reduced in solids content (pigment and solids) to between .25% and 3% either by adding the concentrate to the carrier or by adding the carrier to the concentrate.

Useful toner concentrates have a dilution number of about 4 to 6 while the developer has a dilution number of about 20 to 800, the dilution number being defined as the weight of the carrier divided by the weight of binder.

The above procedure may be utilized to produce a developer which includes a combination of different pigments present in a predetermined ratio as needed to provide any desired hue, shade, chromaticity, covering power, color or reflection.

It is to be understood that similar combinations of pigments of pH less than 6.4 can be used to give negative developers with similar characteristics.

By the present invention, polychrome developers are possible which assure constant color density and hue for a substantial period of time, because each of the individual colored pigments is deposited in an amount proportional to the amount needed to provide the desired color. If the mobility and/or plating-out efficiency of the different colored marking particles differ substantially from each other, a disproportional depletion takes place wherein one or the other pigment is deposited in greater amounts thereby causing a change in color during use of the developer.

The above disadvantage has been overcome in accordance with the present invention by providing pigments having approximately the same pH, and which are surrounded by a resin envelope to provide a marking particle wherein each of the marking particles of different color has substantially the same electrophoretic mobility and plating-out efficiency through the carrier when under the influence of an electrostatic latent image.

Ex.	Pigment	Resin	Polarity	Carrier
1.....	Permanent Red 2B Citation Lt. (Ba) 1058, .01% pigment solids in developer.	Alkyd, Acid No. 8 Visc. F 1+, 65% Soya, 24% Phthalic Anhydride, Pigment resin ratio 1:14.	Positive.....	Odorless mineral thinner.
2.....	Phospho-tungstate Bluegrass Green 3910, .01% pigment solids in developer.	do.....	Negative.....	Do.
3.....	Phthalocyanine, Zulu Green 3826, .01% pigment solids in developer.	do.....	do.....	Do.
4.....	Phthalocyanine, Zulu Blue toner 4852, .01% pigment solids in developer.	do.....	Positive.....	Do.
5.....	Phthalocyanine, Zulu Blue toner 4860, .01% pigment solids in developer.	do.....	do.....	Do.
6.....	Bontone Brown Y 7D-2250, .01% pigment solids in developer.	do.....	do.....	Do.
7.....	Yellow Toner 3D-1840, .01% pigment solids in developer.	do.....	do.....	Do.

One aspect of the present invention relates to coordinating the characteristics of the various pigments, particularly the organic pigments to provide marking particles having substantially the same electrophoretic mobility through the carrier liquid and non-selective plating-out efficiency on the imaging areas. Coordinated mobility is achieved by providing a plurality of pigments capable of providing a developer of a particular polarity and wherein the pH values of the pigments are relatively close to each other. For example, a positive developer

The developers were made by mixing 3 grams of pigment and 6 grams of the above resin (79% solids)¹ with a small amount of carrier and then ground together. Thereafter 54 grams of resin and carrier were added to bring the carrier amount up to 15 grams. The resulting toner paste contained 57% solids with a pigment to binder ratio of 1:14. To form a developer, 0.8 gram of paste were added to 400 ml. of carrier to provide a pigment solids concentration of .01% and a total solids content of 0.15%.

Ex.	Pigment	Resin	Polarity	Carrier
8.....	Benzidene Yellow Toner 3D-2052 .01%.....	Alkyd, Acid #8 Visc. F 1+, 65% Soya, 24% Phthalic Anhydride Pigment resin ratio 1:14.	Positive.....	Odorless mineral thinner.

which gives an image deposit of virtually any color may be provided by mixing in predetermined quantities colored pigments such as a permanent red pigment having a pH of about 8.32, a green-gold pigment having a pH of about 8.23 and a phthalocyanine blue pigment having a pH of about 8.34 as noted in the above table. By mixing predetermined amounts of each of the developers or toner concentrates containing the above pigments in accordance with standard color mixing techniques, the various hues and shades may be provided. Additionally, it is also possible to formulate a developer by initially mixing the preselected amount of pigments and grinding them together to form a toner paste which may be diluted to provide a toner concentrate or when followed by further dilution to provide a developer.

Example 9

To form a polychrome black, 1 gram of each of the pigments used in Examples 1, 5 and 8 were mixed with 6 grams of the above resin and enough carrier to bring the mixture to grinding consistency. The mixture was ground in a friction lid closed can one-third filled with one quarter inch stainless steel shot agitated on a paint shaker and thereafter 54 grams of resin and 30 grams of carrier were added to form a toner paste in which the pigment to binder ratio was 1:14. One gram of paste was diluted with 400 ml. of carrier and prints formed. The developer fixed well on the image bearing surface upon removal of

¹ The resin is supplied as a solution of 70% solids.

9

the carrier, there was no smudging and the print squeezed well. The print exhibited good line density, no hollow lines or halo and the black print exhibited a slight green tint.

Example 10

Separate toner pastes were made using the pigments of Examples 1, 5 and 8, and the toner pastes were mixed to form various colors, for example, red and blue, and red, blue and yellow. The resultant mixed toner pastes were diluted to form developers and the prints made therefrom showed essentially the same characteristics as in Example 9.

Other colors were formed by mixing the pastes, for example a brown from 1059 red, 4860 blue and 3 D-2052 yellow; green from 3 D-2052 yellow and 4860 blue. After mixing the pastes, the resultant mixture was diluted to developer consistency. The resolution of the developed print was 70 lines per mm. Instead of mixing toner paste, the developer may be mixed to achieve the same result.

Example 11

A negative polychrome black was formed from three negative pigments, i.e., 0.9 gram of each of Pyrazell Red toner 1-D 1970, Permanent Green 3 D-8322 and 1.2 grams of Phthalocyanine-Zulu Blue Floc resistant 4863. The toner paste included 60 grams of the above resin and 11 grams of carrier, and 0.8 gram of paste were diluted in 400 ml. of carrier to provide a developer. Prints were made from positive and negative transparencies using the above formulation.

Example 12

Pastes were separately compounded as previously described and the following amounts of separate pastes were mixed, 0.44 gram of red 1 D-1970, 0.31 gram of green 30-8322 and 0.65 gram of blue 4863. The resultant paste was mixed and added to 400 mls. of carrier to provide a negative black developer which performed well.

Example 13

A negative green developer was made by mixing toner pastes made from 3 D-2052 yellow and 4860 blue.

Example 14

A negative brown developer was made by mixing toner pastes from 1059 red, 4860 blue and 3 D-2052 yellow.

Example 15

Five color reproductions were made from positive developers as above described and deposited in the following color sequence: black, green, brown, blue and red.

Example 16

Five color reproductions were made from negative developers described above and deposited in the order noted in Example 15.

Example 17

Three grams of an organic blue pigment, 10.7 grams of the resin noted in Example 1 and 22.8 grams of carrier were mixed as previously described to form a toner paste. Thereafter, aliquots of carrier were added to the paste until the total amount added was 273 grams, and phase inversion took place as previously described. The resultant material was a toner concentrate of which 2.5 grams were added to 400 mls. of carrier to form a developer having 0.01% pigment solids by weight and a pigment to binder ratio of 1:25.

10

Example 18

The procedure described in Example 17 was followed using 3 grams of pigment, 21 grams of binder, 22 grams of carrier to form the toner paste, with the toner concentrate being formed by the addition of 254 grams of carrier as previously described. The pigment to binder ratio was 1:5.

Example 19

A developer having a pigment to binder of 1:10 was formed as follows: 3 grams of pigment, 42 grams of resin and 22.8 grams of carrier were processed to form a toner paste, with the toner concentrate being formed by the addition of 233 grams of carrier. The developer was formed by diluting 2.5 grams of toner concentrate with 400 mls. of carrier. A print developed with this developer showed good fixing properties, lines were filled and little if any pigment was removed during the squeegee operation.

Example 20

The toner paste was formed from 3 grams of pigment, 75 grams of resin of Example 1 and 30 grams of carrier. The toner concentrate was formed by the addition of 192 grams of carrier to provide a material having a pigment to binder ratio of 1:21. A toner paste was formed from 1.5 grams of resin and 45 grams of carrier. The toner concentrate was formed by the addition of 103 grams of carrier to provide a pigment to binder ratio of 1:70. Prints made with this developer exhibited good fixing, drying, squeegeeing and the lines were filled in.

Example 21

A polychrome organic black developer having a pigment to binder ratio of 1:2.5 was made as follows: 1 gram of Permanent Red-2B, Citation Med. Yel. 1059, 1 gram of Phthalocyanine-Zulu Blue 4860 and 1 gram of Benzidine Yellow Toner 3 D-2052 were milled with 7 grams of resin and enough carrier to provide grinding consistency. Thereafter 100 grams of resin were added with an additional 237 grams of carrier to provide a toner concentrate. 3½ grams of concentrate were diluted with 400 mls. of carrier to provide a positive polychrome black having a pigment to binder ratio previously described.

By matching the pH of the pigment as closely as possible, it was noted that the developer did not suffer from disproportional depletion of the individual color components thereof and provided a developer in which the individual color particles were deposited in essentially the proper proportion.

Example 22

One such developer includes 1 gram of red pigment 1059 with a pH of about 8.4, 1 gram of 3 D-2052 with a pH of about 6.9 and 1 gram of pigment 4852 with a pH of about 8.3. 86 grams of the resin of Example 1 were mixed with 26 grams of carrier and the pigment resin and carrier were milled together. Thereafter 60 grams of resin and 15 grams of carrier were added to provide a toner paste, with the concentrate being formed with the addition of 110 grams of carrier to provide a concentrate having a 21.5% solids content. 4.2 grams of the concentrate were added to 400 mls. of carrier to provide a developer having a pigment concentration of 0.01%. Pigment to resin ratio was 1:20, and tests indicated there was no disproportional depletion of the respective pigment components.

The following specific examples are illustrative of vari-

ous developer compositions in accordance with the present invention:

This operation, if it is used, would be carried on preferably prior to the squeegee operation or whatever other opera-

Ex.	Pigment	Resin	Polarity	Carrier
23.-----	3 grams Pure Yellow Iron Oxide YLO-1883B.	81 grams of resin of Example 1, pigment to resin ratio 1:20.	Positive-----	Odorless Mineral Thinner.
24.-----	3 grams Pure Red Iron Oxide R-8098.	do.	do.	Do.
25.-----	3 grams of Raw Umber RU 80-46.	do.	do.	Do.
26.-----	3 grams Hydrated Chrome Green Oxide GH 9869.	do.	do.	Do.
27.-----	3 grams Pure Kroma Red Oxide RO 3097.	do.	do.	Do.
28.-----	3 grams Pure Red Iron Oxide R-2899.	do.	do.	Do.
29.-----	3 grams Pure Chromium Green Oxide G-6099.	do.	do.	Do.
30.-----	3 grams Burnt Umber VVF BU 5250F.	do.	do.	Do.
31.-----	3 grams Burnt Umber VVF BU 5452.	do.	do.	Do.
32.-----	3 grams Magnetic Oxide IRN-351.	do.	do.	Do.
33.-----	3 grams Magnetic Oxide IRN-100.	do.	do.	Do.

Each of the above developer compositions is relatively stable in that the dispersed phase does not tend to permit the pigment to settle out, agglomerate or merge into stratified distinct layers of resin and pigment, and carrier primarily because of the relationship between the resin and the K-B value of the carrier liquid. While the marking particles including the pigment and resin may settle to the bottom of a container after extended storage, they settle as a dispersed phase and may be easily uniformly dispersed in the carrier liquid simply by stirring or shaking the composition. Care should be taken however to prevent excessive shear which tends to strip the resin from the pigment.

Development of an electrostatic latent image may be by immersion of the image carrier in the developer through brushing, dipping, rolling, spraying or the like followed by removal of the carrier liquid from the image surface to effect substantially permanent adhesion of the deposited marking particles preferably by oxidation or other reaction of the resin component thereof. As the individual marking particles are attracted toward the surface and deposited thereon as controlled by an electrostatic latent image through the influence, pull or force of the electrostatic field, the concentration of resin relative to carrier liquid on the image areas increases substantially to form a substantially continuous film by means of a phase inversion or the destruction of the organosol in which a relatively small amount of carrier liquid is retained in the resin film. The film formed by the resin of the developer may in some areas of the print be continuous to the extent that it is lattice-like in nature as opposed to a substantially pin-hole free layer. After removal of a substantial portion of the carrier liquid or the continuum, the image may be fixed to provide a substantially permanent image which is resistant to smudging and insoluble in hydrocarbon vehicles because of the oxidation of the resin component of the marking particle.

The phase inversion from a dispersed phase to a continuous phase in combination with the electrostatic forces of deposition is advantageous because it allows mechanical removal of substantial amounts of mechanically deposited marking particles which have not undergone phase inversion as well as carrier liquid or continuum from the image bearing surface by a squeegee roller or the like which is in pressure contact with the image bearing surface and the developed image thereon. Little, if any, splitting or off-setting of the image takes place, and the deposited film of marking elements appears to be adhered to the image areas sufficiently to allow some mechanical handling of the image bearing surface without substantial distortion of the image deposit. Following removal of a substantial portion of the depleted developer, carrier liquid or continuum, substantially permanent fixing may be accomplished by air drying. If no squeegee is used, the carrier liquid may be removed by air drying or the like to fix the developed image.

If desired, clear carrier liquid may be utilized to rinse away any marking elements which may have been mechanically or gravitationally deposited in the non-image areas.

tion is used to remove the continuum or carrier mechanically. Also, in accordance with the present invention, it is possible to treat the image bearing surface with the electrostatic latent image thereon with clear carrier liquid of the type previously described, and thereafter develop the latent image with any of the developer compositions noted above to minimize undesired chemical, mechanical, electrical or other physical interactions between the developer and the image bearing surface.

The liquid developer of the present invention may also be used in a reversal development procedure wherein the surface of the image bearing member is charged and exposed to form a pattern of one polarity, for example negative, and the surface is treated with a negative developer which is attracted to the areas of the surface other than negatively charged areas as is well understood in the art.

By the present invention, it is possible to provide a series of toner concentrates and developer compositions having substantially the same basic characteristics except for the color of the pigment. In this way, mixing of any individual pigments to provide toner concentrates and developers of different color is possible and at the same time, by matching the pH values of the pigments as previously noted, the problem of disproportional depletion of selected color components of the developer is substantially eliminated. The toner concentrate of the present invention may be stored for relatively long periods of time in sealed cans since the resin is substantially completely surrounded by carrier liquid and thus maintained out of contact with air. In addition, when using the developer of the present invention the concentration control thereof is simplified by the fact that carrier may be added to a developer mixture or additional toner concentrate may be added to the developer mixture without destroying the emulsified or dispersed condition either of the developer or of the added toner concentrate.

The use of organic pigments is preferred in accordance with the present invention particularly when the developer of this invention is to be used in the formation of multi-color images. Since the organic pigment developers are generally transparent in nature, and the same or compatible resins may be used, over-printing techniques may be employed with the improved developer, and deposition of one resin over another, as by deposition of one developer over another presents no major problems since the resin components thereof are compatible.

The pigment components perform the function of constituting a nucleation center for the resin, and thus the combined characteristics of carrier, resin and pigment mutually cooperate to provide a self-fixing developer having a stable polarity.

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 examples and methods, as well as pre-

ferred embodiments thereof, and it is not intended that such details be regarded as limitations upon the scope of the invention except so far as is included in the accompanying claims.

What is claimed is:

1. The method of developing an electrostatic latent image on an image bearing member with an emulsified two-phase liquid developer wherein said developer includes a first and second group of marking elements dispersed in an electrically insulating carrier liquid, each of said marking elements of both groups having a characteristic charge of substantially the same polarity for deposition on a surface as controlled by the electrostatic charge thereon, each said marking element comprising as the essential ingredients a pigment and a liquid resin, said liquid resin being selected from the group consisting of oil modified alkyd resins, oleo resin varnish, also resinous vinyl polymers and copolymers, the pigment of the first group of marking elements being different in color from the pigment of the said second group of marking elements, said resin forming a two-phase system of carrier and marking elements and being characterized by the formation of an emulsion in the presence of said carrier above a predetermined ratio of carrier to resin, said pigments being present in a predetermined ratio by weight and being characterized by a polarity and electrophoretic mobility in said carrier which is a function of the pH of each said pigment in an aqueous medium, the polarity of said pigments being positive at a pH above 6.4 and being negative at a pH below 6.4, the pH of each of said different pigments being relatively close to each other to provide marking particles having essentially the same electrophoretic mobility in said carrier, said method comprising the steps of contacting the surface of said image bearing member having an electrostatic latent image thereon with said liquid developer, said electrostatic charge image creating field conditions causing migration of said marking elements through said carrier at an electrophoretic mobility rate which is a function of the pH of each said pigment and proportional deposition thereof on said image bearing surface in a ratio substantially the same as said predetermined ratio to maintain color balance of said developer and developed image, the deposition of said marking elements on said image bearing surface under the influence of said electrostatic latent image operative to increase the concentration of resin in the area of deposition of said marking elements thereby decreasing the ratio of carrier to resin below said predetermined minimum, the increase in concentration of the resin operative to form a continuous phase of resin and carrier and an essentially continuous film of resin, and removing the carrier to effect adhesion of said resin to provide a substantially permanent developed image thereon.

2. The method as set forth in claim 1 wherein each of said different pigments has a pH greater than 6.4 and wherein the polarity of said different pigments is positive.

3. The method of developing an electrostatic latent image on an image bearing member with a liquid developer wherein said developer includes a first and second group of marking elements dispersed in an electrically insulating carrier liquid having a K-B value of between 20 and 70, each said group of marking elements compris-

ing as the essential ingredients a pigment and a resin, said resin forming a two-phase system of carrier and marking elements and being an oil modified alkyd resin characterized by the formation of an emulsion in said carrier when diluted to between 4 and 800 times the weight thereof with a carrier liquid having a K-B value of between 20 and 70, the pigment of the first group of marking elements being different in color from the pigment of said second group of marking elements, the solids content of said developer being between about .25% and 3% by weight and the total pigment to resin ratio by weight being between 1:2.5 and 1:70, said pigments being present in a predetermined ratio by weight and being characterized by a polarity and electrophoretic mobility which is a function of pH in an aqueous medium, the polarity of said pigments being positive at a pH above 6.4 and being negative at a pH below 6.4, the pH of each of said different pigments being relatively close to each other to provide marking particles having essentially the same electrophoretic mobility in said carrier, said method comprising the steps of contacting the surface of said image bearing member having an electrostatic latent image thereon with said liquid developer, said electrostatic charge causing migration of said marking elements through said carriers at an electrophoretic mobility rate which is a function of the pH of said pigment and proportional deposition thereof on said image bearing surface in a ratio substantially the same as said predetermined ratio to maintain color balance of said developer and developed image, the deposition of said marking elements on said image bearing surface under the influence of said electrostatic latent image operative to increase the concentration of resin in the area of deposition of said marking elements thereby decreasing the ratio of carrier to resin below a ratio of 4:1, the increase in concentration of the resin operative to form a continuous phase of resin and carrier and an essentially continuous film of resin, and removing the carrier to effect adhesion of said resin to said image bearing surface to provide a substantially permanent developed image thereon.

4. The method as set forth in claim 3 wherein each of said different pigments has a pH greater than 6.4 and wherein the polarity of said different pigments is positive.

References Cited

UNITED STATES PATENTS

2,891,911	6/1959	Mayer et al.	117—37
2,907,674	10/1959	Metcalfe et al.	117—37
3,058,914	10/1962	Metcalfe et al.	252—62.1
3,076,722	2/1963	Greig	252—62.1
3,078,231	2/1963	Metcalfe et al.	252—62.1
3,080,251	3/1963	Claus	117—37
3,084,043	4/1963	Gundlach	117—37
3,102,026	8/1963	Metcalfe et al.	117—37
3,104,169	9/1963	Metcalfe et al.	117—37
3,198,649	8/1965	Metcalfe et al.	117—37
3,241,957	3/1966	Fausser et al.	117—37
3,244,633	4/1966	Yellin et al.	252—62.1

60 WILLIAM D. MARTIN, *Primary Examiner*.

MURRAY KATZ, *Examiner*.

E. J. CABIC, *Assistant Examiner*.