United States Patent

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[15] 3,669,886

[45] June 13, 1972

[54] LIQUID DEVELOPER FOR ELECTROSTATOGRAPHY

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[22] Filed: Sept. 11, 1968

[21] Appl. No.: 767,031

Related U.S. Application Data

[63] Continuation-in-part of Ser. No. 397,638, Sept. 18, 1964.

[52] U.S. Cl. ..... 252/62.1, 117/37 LY

[51] Int. Cl. G03g 9/04

[58] Field of Search ..... 252/62.1; 117/37 LY

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[57] ABSTRACT

A liquid electrostatographic image developer composed of the following five constituents; a petroleum fraction paraffinic solvent, a solid film-forming fixing agent, a solid dispersant, a solid charge director, and a submicron solid electroscopic pigment material. The fixing agent and the dispersant are dissolved in the solvent. The charge director is carried by the solvent being either dispersed or dissolved therein. The pigment material is insoluble in the solvent and is dispersed therein. The solvent evaporates at least as fast as kerosene and slower than hexane; it has a K.B. number less than 35, a dielectric constant less than 3½, a flash point of at least 100° F, and a room temperature viscosity of between 0.5 and 2.5 centipoises. The solvent is non-toxic, practically odorless, highly resistant, and non-polar; it evaporates rapidly slightly below the char point of paper. The film-forming fixing agent is non-tacky and forms a tough film; it has a good solvent release and it forms, upon evaporation of the solvent, a coherent film that binds the pigment material in place, and bonds well to an electrostatographic surface.

3 Claims, No Drawings

LIQUID DEVELOPER FOR ELECTROSTATOGRAPHY

RELATED APPLICATION

This application is a continuation-in-part of application Ser. No. 397,638 filed Sept. 18, 1964.

BACKGROUND OF THE INVENTION

1. Field of the Invention

Electrostatographic liquid developers.

2. Description of the Prior Art

The use of liquid developers for electrostatography, i.e., rendering visible as a permanent image a latent image consisting of a pattern of electrostatic charges, is well known. Advocates thereof prefer it over the dry method for developing such a pattern of charges for many reasons, including, for example, sharper and better defined images, images having a higher degree of and more delicate gradations of contrast, cleaner whites, more economical use of the developer, a faster developing cycle, and simpler, less expensive and more trouble-free developing equipment. However, although the industry strongly desires an excellent liquid electrostatographic developer, those which presently are commercially available or which have been proposed in patent literature and in publications are subject to sundry deficiencies that are largely concerned with refinements of commercial demands. For example, the liquid developers heretofore proposed have not given sufficiently good resolution or sufficiently dense or sharp images. Where the final image was black, it was not black enough, nor was the background sufficiently clear. Moreover, as to many developers, there has been a serious complaint that the shelf life was not long enough in that some solids suspended within the liquid developer tended to settle and agglomerate too quickly, making it necessary to redisperse them prior to use. This sometimes could be accomplished by vigorous hand shaking, but was not too satisfactory. Other solids settled in the form of a cake which could not be redispersed by manual or even machine shaking and which had to be resuspended by passing the ingredients of the developer through a milling machine or the like, e.g., a ball mill or pebble mill. Still further, other liquid developers have tended to gel and thereby become ineffective when subjected in bulk to mild temperatures, e.g., in the order of 125° F, such as might be encountered in electrostatographic developing equipment.

SUMMARY OF THE INVENTION

It is a principal object of the present invention to provide a liquid electrostatographic image developer which overcomes the aforesaid deficiencies and drawbacks, effecting through its use a consistently and commercially acceptable developed electrostatic image.

More particularly, it is an object of the present invention to provide a liquid electrostatographic image developer which will secure a dense image of good resolution, an image which, when black and white copy is to be made, is composed of blacks that are of a deep jet hue.

It is another object of the invention to provide a liquid electrostatographic image developer which will create a visible image that is bonded firmly to the sheet on which the electrostatic pattern of charges was present, for example, which will bond well to a sheet coated with a photoconductive material such as zinc oxide or zinc sulfide or to a sheet of a non-photosensitive insulating material.

It is another object of the invention to provide a liquid electrostatographic image developer which will form a fast-drying non-tacky, non-smearing and non-offsetting image, and which will enable an apparatus utilizing the same to have a rapid developing and drying cycle.

It is another object of the invention to provide a liquid electrostatographic image developer, which, in addition to its many desirable attributes, is inexpensive and easy to produce.

Bearing in mind that equipment employing a liquid electrostatographic image developer may be run in an enclosed area under the supervision of an operator, it is another object of the invention to provide a liquid electrostatographic image developer which is odorless, non-toxic and non-flammable under the conditions of use.

It is another object of the invention to provide a liquid electrostatographic image developer which will not settle or separate upon standing for extended periods and which will not gel in a developing machine under normal conditions of use.

Other objects of the invention in part will be obvious and in part will be pointed out hereinafter.

The invention accordingly consists in the compositions of matter which will be exemplified in the materials hereinafter described and of which the scope of application will be indicated in the appended claims.

In general, the several objects of the invention are accomplished by providing a liquid electrostatographic image developer which essentially consists of an organic liquid carrier constituting a petroleum fraction in which there are dissolved a solid film-forming fixing agent, i.e., a binder, and a solid dispersant, in which a solid charge director is dissolved or dispersed, and in which a finely divided solid opaque electroscopic material that functions as a pigment is dispersed. The film-forming agent and the dispersant constitute the major proportion of the solid constituents of the liquid electrostatographic image developer and since they are fully dissolved in the organic liquid carrier, they will not settle out upon standing. However, even though present in dissolved form, they perform their primary functions efficiently, that is to say, the dispersant will maintain the pigment and also the charge director, if the latter is dispersed, in suspended state despite the fact that the dispersant is in solution, and the film-forming fixing agent will act to bind the electrostatically attracted pigment to an electrostatic electrophotographic or an electrostatic electrographic base sheet after the carrier has evaporated. The solid charge director and the solid pigment are present in minor proportions and will remain in suspension indefinitely.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

The organic liquid carrier is, as mentioned above, a petroleum fraction, it having been discovered that this particular class of carriers is uniquely capable of effecting the present invention by virtue of the following attributes: (a) quick evaporation, e.g., a thin film of the carrier will evaporate in a few seconds at a temperature below the char point of paper, so as to permit fast drying; (b) non-toxicity; (c) low odor; (d) the characteristic that when employed with soluble solid film-forming agents it will fully escape therefrom so as to leave the solid film deposited by such agent tack-free and not subject to evaporation over protracted periods of time after the deposited image is seemingly dry; (e) sufficient fluidity to allow the particles of pigment to migrate therethrough with ease so that the pigment is capable of being quickly electrostatically attracted to and coupled with the pattern of electrostatic charges which is to be developed; (f) not attacking the coating binders on a base sheet and not attacking other ingredients of the sheet; (g) not bleeding the electrostatic charges before the pigment is deposited so as to maintain any desired degree of contrast; and (h) inexpensiveness.

In order to obtain these beneficial attributes, the petroleum fraction, i.e., paraffinic solvent, should have an evaporation rate at least as fast as that of kerosene, but slower than that of hexane. Thereby, the evaporation of the liquid from a film will be rapid, e.g., 2 seconds, at a temperature slightly below the char point of paper, it being customary to raise the temperature of the film of liquid developer to this level for the purpose of evaporating the developer after the opaque electroscopic particles of pigment have been deposited by attraction on the electrostatically charged pattern. The petroleum fraction should have a low K.B. (Kauri-butanol) number, to wit, less than 35, and preferably between 26 and 35. This low K.B.

number minimizes the possibility that the petroleum fraction will attack the coating binder, e.g., the binder for the zinc oxide, or will attack any sizing on the sheet, e.g., paper, upon which the coating is applied. The petroleum fraction also should be substantially free of aromatic liquid constituents, i.e., it should be substantially aromatic-liquid-free. This term, as used herein, connotes that the proportion of aromatic liquids in the organic liquid carrier should not be in excess of two per cent by weight. The aromatic liquids have a strong tendency to attack the coating binders, e.g., the coating binders for zinc oxide, but in concentrations of less than two per cent this tendency is so negligible as to be unnoticeable. The petroleum fraction must have a high electrical resistivity, e.g., in the order of at least 10^9 ohm centimeters, and a dielectric constant of less than 3½, so that the liquid carrier will not dissipate the pattern of electrostatic charges which are to be developed. The TCC (Tagliabue closed cup) flash point of the liquid carrier should be at least 100° F and preferably about 120° F to 152° F, whereby under the conditions of use the liquid is considered non-flammable. The paraffinic solvent also is non-toxic. It possesses no objectionable odor and preferably is odor-free, this being denoted by the term "low odor." Consonant with its low dielectric constant and high resistivity, the liquid carrier is non-polar. The liquid carrier should have low viscosity for the purpose, as indicated above, of permitting rapid migration therethrough of opaque electroscopic charged pigment particles which are to be attracted in large number to the electrostatically charged image which is to be developed. Such viscosity should be between 0.5 and 2.5 centipoises at room temperature. The petroleum fraction also is inexpensive.

Examples of petroleum fraction organic liquid carriers having physical characteristics which fall within the foregoing criteria are Shell Sol 71, manufactured by Shell Oil Company; Isopar H, Isopar K, and Isopar L, manufactured by Humble Oil and Refining Company; Amsco OMS, Amsco 460 Solvent and Amsco Odorless Insecticide Base manufactured by American Mineral Spirits Company; and odorless kerosene. All of the foregoing are low odor paraffinic solvents. The dielectric constant of Shell Sol 71 is 2.06 at room temperatures. The other solvents have dielectric constants of the same order of magnitude. Other physical characteristics of Shell Sol 71, Isopar H, Isopar K, Isopar L, Amsco OMS, Amsco 460 Solvent and Amsco Odorless Insecticide Base which fingerprint these solvents and denote the presence of several of the above listed attributes are set forth below:

	Distillation		Flash point			
	IBP,* ° F.	Dry end point, ° F.	° F. TCC	K.B. No.	Aniline point, ° F.	Specific gravity 60°/60° F.
Shell Sol 71	345	398	121	26.5	183	0.7563
Isopar:						
H	350	371	123	26.9	183	0.7571
K	349	383	126	26.5	185	0.7587
L	372	406	144		187	0.7674
Amsco:						
OMS	352	386	125	27.0	184.5	0.7608
460 solvent	375	456	150	34.5	146.5	0.8108
Odorless insecticide base	375	482	152	26.5	175.0	0.7711

*Initial Boiling Point ASTM D-1078.

The pigment employed can be any one of the many now known to the art in connection with liquid electrostatographic developers. As is well-known, these pigments essentially constitute very fine solid particles the size of which is in the submicron range, which are opaque in mass and which are capable of acquiring an electroscopic charge. They are insoluble in the liquid carrier. So many different kinds and species of pigments are known that only typical representative examples will be mentioned. These are: powdered metals, e.g., powdered aluminum; powdered metal oxides, e.g., powdered magnetic iron oxide; powdered metal salts, e.g., powdered cadmium selenide (CdSe), powder lead iodide (PbI_2), powdered lead chromate ($PbCrO_4$); Cyan Blue G.T. 55-3295 (American Cyanamid Company, Pigments Division)*(material in first parentheses indicates name of manufacturer.) (74160)**(**material in second parentheses indicates color index number.) described in United States Letters Patent No. 2,486,351; Cibacron Black BG (Ciba Company, Inc.); Cibacron Turquoise Blue G (Ciba); Cibalon Black BGL (Ciba); Orasol Black BRG (Ciba); Orasol Black RBL (Ciba); Acetamine Black CBS (E. I. du Pont de Nemours and Company, Inc.); Crocein Scarlet N Ex (duPont) (27290); Fiber Black VF (duPont) (30235); Luxol Fast Black L (duPont) (Solv. Black 17); Nigrosine Base No. 424 (duPont) (50415 B); Oil Black BG (duPont) (Solv. Black 16); Rotalin Black RM (duPont); Sevron Brilliant Red 3 B (duPont); Basic Black DSC (Dye Specialties, Inc.); Hectolene Black (Dye Specialties); Azosol Brilliant Blue B (General Aniline and Film Corporation, Dyestuff and Chemical Division) (Solv. Blue 9); Azosol Brilliant Green BA (General Aniline) (Solv. Green 2); Azosol Fast Brilliant Red B (General Aniline); Azosol Fast Orange RA Conc. (General Aniline) (Solv. Orange 20); Azosol Fast Yellow GRA Conc. (General Aniline) (13900 A); Basic Black KMPA (General Aniline); Benzofix Black CW-CF (General Aniline) (35435); Cellitazol BNFV Ex Soluble CF (General Aniline) (Disp. Black 9); Celliton Fast Blue AF Ex Conc (General Aniline) (Disp. Blue 9); Cyper Black IA (General Aniline) (Basic Blk. 3); Diamine Black CAP Ex Conc (General Aniline) (30235); Diamond Black EAN Hi Conc. CF (General Aniline) (15710); Diamond Black PBBA Ex (General Aniline) (16505); Direct Deep Black EA Ex CF (General Aniline) (30235); Hansa Yellow G (General Aniline) (11680); Indanthrene Black BBK Powd. (General Aniline) (59850); Indocarbon CLGS Conc. CF (General Aniline) (53295); Katigen Deep Black NND Hi Conc. CF (General Aniline) (53190); Nyliton Black B (General Aniline); Palatine Fast Black WANA Conc. CF (General Aniline) (15711); Rapidogen Black 3 G (General Aniline) (Azoic Blk. 4); Sulphon Cyanine Black BA-CF (General Aniline) (26370); Zambezi Black VD Ex Conc. (General Aniline) (30015); Azo Oil Black (National Aniline Division of Allied Chemical and Dye Corporation) (Solv. Blk. 12); Iosol Blue 6 G (National Aniline) (Solv. Blue 30); Spirit Nigrosine SSB (National Aniline) (50415); Methyl Violet T Lake (N.Y. Color and Chemical Co.) (42535); Rubanox Red CP-1495 (The Sherwin-Williams Company) (15630); Victoria Blue Molybdate Lake (Standard Ultramarine and Color Co.) (42595); Toner 8100 (Paul Ulich and Company, Inc.) a mixture of carbon black and black dye precipitated on a lake; Raven 11 (Columbian Carbon Company) carbon black aggregates with a particle size of about 25 μ, and chrome green.

The solid film-forming fixing agent, in addition to being fully soluble in the liquid carrier must have a good solvent release characteristic, that is to say, must permit the solvent to evaporate completely and quickly through a solid coherent film-like deposit left as a residue by solvent evaporation. The film thus deposited must be tack-free, tough and coherent, whereby the final image that is formed will not smear or shred. The film-forming agent must be compatible with the binder for the electrostatographic coating, e.g., with the binder for a photoconductive zinc oxide coating, and should bond well to said coating in order to avoid any tendency of the finished

image to separate or peel from the coated sheet.

An excellent film-forming agent having the foregoing characteristics is a hydrogenated polymerized rosin, a typical example being Resin NC 11, manufactured by Hercules Powder Company. This is a pale thermoplastic acidic wood rosin resin that has been both polymerized and hydrogenated. It has a softening point of 85°C to 93°C by the Hercules drop method and an acid number of 145-65. Its density at 20° C is 1.065. It has a saponification number of 155–165. Its degree of hydrogenation is about 90 percent and it has an average molecular weight of 360. About 20 percent of the rosin acids are polymerized.

Other useful film-forming agents are:

Resin	Manufacturer	Description	Acid No.	Softening pt., ° C.[1]
Lewisol 7	Hercules	Glycerol ester of modified wood rosin	8	168 HDM
Pentalyn:				
A	do	Pentaerythritol ester of wood rosin	12	111 HDM
C	do	Pentaerythritol ester of polymerized wood rosin	14	135 HDM
G	do	Modified pentaerythritol ester of wood rosin	14	135 HDM
H	do	Pentaerythritol ester of hydrogenated wood rosin	13	104 HDM
K	do	Pentaerythritol ester of dimeric resin acids	14	192 HDM
X	do	Modified pentaerythritol ester of wood rosin	14	159 HDM
860	do	Pentaerythritol ester of dimeric resin acids	15	172 HDM
Polypale Ester 10	do	Glycerol ester of polymerized wood rosin	6	112 HDM
Staybelite Resin	do	Hydrogenated wood rosin	165	76 HDM
Picco 6120–3	Pennsylvania Industrial Chemical Company.	Petroleum hydrocarbon from the polymerization of dienes and olefins derived from crude petroleum stock.	<1	120 R&B
Krumbhaar 484	Lawter Chemicals, Inc., Krumbhaar Resin Division.	Pentaerythritol ester of modified wood resin	<1	180–190 MM
Nevchem 100	Neville Chemical Company	(+)		

[1] HDM=Hercules Drop Method; R&B=Ring and Ball; MM=Mercury method.

+A thermoplastic petroleum hydrocarbon resin in which the units in the polymer are predominantly aromatic or cyclic in structure. It is prepared by the polymerization of unsaturated hydrocarbon fractions boiling between about 125° C and about 250° C, having a Sp. Gr. (15.6/15.6° C) of between 0.90 and 0.95. The polymerizable constituents comprise between about 30 and 90 percent by weight and the principal polymerizable monomers are:

cyclodiene dimers**	5–30%
indene	5–20%
vinyl toluene	5–25%
styrene	0–10%

**Such as dicyclopentadiene (C_{10}); di-methylcyclopentadiene (C_{12}); codimer of cyclopentadiene and methylcyclopentadiene (C_{11}).

The balance dry weight of the hydrocarbon fraction is constituted of essentially umpolymerizable paraffins, napthenes and aromatics containing eight or more carbon atoms per molecule and boiling within the aforementioned range, i.e., between about 125° and 250° C.

The unsaturated hydrocarbon fractions from which the resin is obtained come from high temperature and low pressure pyrolysis of normally liquid or gaseous hydrocarbons having two or more carbon atoms per molecule. The cracking operation may be by-products of pyrolytic processes in which the principal products sought are low boiling olefines and dienes such as ethylene, propylene, butenes, butadiene, etc. which are widely used base hydrocarbons in the petrochemical and plastics fields including elastomers. Pyrolysis of both liquid and gaseous hydrocarbons for such purposes is well known and need not be described in detail.

Test Property	Nevchem 100 (Typical properties)
1. Soft Point (R&B) °C.	100
2. Molecular Weight (No. Ave)	800
3. C/H Weight ratio	10.5
4. Sp. Gr. 25/25°C	1.090
5. Refr. Index 25°C/D	1.602
6. Iodine Number	65
7. Acid Number	<1

List of Test Methods:
1. ASTM E–28–58T
2. Osmotic
3. Combustion Analysis
4. ASTM D–71–52
5. Neville Method (toluene solution, extrapolated to solid resin)
6. ASTM D–555

The solid dispersant, like the solid film-forming agent, is characterized by its full solubility in the paraffinic solvent carrier. It must disperse solid pigments of sub-micron range in a non-polar solvent. It must be compatible in solid form with the solid film-forming agent and desirably is a film-forming agent in its own right. Desirably, likewise, it will augment the charge direction of the solid submicron pigment particles.

Examples of solid dispersants having the foregoing physical characteristics are: Lube Oil 564 and FOA 2. Lube oil 564 is manufactured by du Pont and is composed of 40 percent of methacrylate polymer and 60 percent of light neutral petroleum oil. FOA2 is manufactured by du Pont and is composed of 50 percent of methacrylate polymer and 50 percent of kerosene. Insofar as the above examples of dispersants are concerned, it is the solid constituent that constitutes the dispersant, the liquid carrier merely forming a convenient vehicle therefor. Other dispersants include: an oil additive constituting a tripolymer prepared from a weight mixture of 50 parts of octadecenyl methacrylate, 10 parts diethylaminoethyl methacrylate, and 40 parts styrene, the same being polymerized by conventional bulk, solution or dispersion polymerization methods involving known initiators including oxygen-yielding compounds, such as benzoyl peroxide, and azo compounds such as alpha, alpha' azodiisobutyronitrile. The polymerization process preferably is carried out in an inert atmosphere, for example, nitrogen or carbon dioxide, at conventional temperatures ranging, as is well known, from 30° to 150° C, depending on the catalyst used, and generally between 50° to 70° C where the catalyst is alpha, alpha' azodiisobutyronitrile. The polymerization is carried substantially to completion to eliminate substantially all of the unpolymerized monomers, it being understood that "substantially to completion" as used herein denotes that there is a remainder of from 0 to 15 percent of total monomers. The aforesaid tripolymer is dissolved in kerosene in proportions of 50 percent by weight of the tripolymer to 50 percent by weight of kerosene. The tripolymer constitutes, as is seen, several completely organic compounds combined in proportions to effect the optimum balance between polar-active and oil-soluble groups. The said tripolymer is large and has an average molecular weight of 50,000.

Still other dispersants that may be used are those disclosed in U.S. Pat. No. 3,048,544, namely alkyl methacrylate maleic anhydride polymer, maleimide polymer, a polymer constituting the reaction product of alkyl methacrylate, polyethylene

glycol methacrylate and maleic anhydride, and a polymer constituting the reaction product of alkyl methacrylate, polyethylene glycol methacrylate and imide of maleic anhydride, and tetraethylene pentamine; the polyglycol substituted polyesters disclosed in U.S. Pat. No. 3,083,187; and the polyglycol substituted polyamides disclosed in U.S. Pat. No. 3,083,188. The methods of preparation of these latter dispersants are detailed in said patents.

The charge directors which are per se well known in the field of liquid electrostatographic image developers must be soluble or dispersible in the paraffinic solvent and must create or augment an electrostatic charge on the sub-micron pigment particles. Examples of useable charge directors pursuant to this invention are: aluminum stearate; aluminum dresinate; vanadium dresinate; tin dresinate; cobalt salt of 2-ethyl hexoic acid; iron salt of 2-ethyl hexoic acid; manganese salt of 2-ethyl hexoic acid; manganese linoleate 1-[2-hydroxyethyl]-2-[mixed pentadecyl and heptadecyl]-2-imidazoline; and Nopco FOA 2, manufactured by Nopco Chemical Company, a fatty amide condensate.

The dresinates are prepared by adding a solution of the corresponding metallic sulfate, e.g., $Al_2[SO_4]_3$, $Sn[SO_4]_2$ or $V_2O_4[SO_3]_3$. $16H_2O$ to a solution of the sodium salt of a processed rosin, to wit, Dresinate 731, manufactured by Hercules Powder Company.

As has been mentioned earlier herein, the major proportion of the solid constituents of a liquid electrostatographic image developer pursuant to the present invention are soluble in the petroleum fraction organic liquid carrier. These constituents are the film-forming fixing agent and the dispersant. The minor proportion or the solids need not be soluble in the liquid carrier, such constituents constituting the necessarily nonsoluble submicron pigment particles and the charge director, the latter optionally being soluble. Thereby, even in concentrated forms of the liquid electrostatographic image developer, prior to dilution, the dispersed particulate solids will not settle upon standing.

The various constituents of the liquid electrostatographic image developer are chemically inert to one another at ambient temperatures, all said constituents being selected and admixed solely for their physical characteristics and not for chemical interaction. Moreover, all of the constituents are heat stable under ambient conditions and a developer made of the foregoing constituents will not gel under the operating conditions prevailing in a liquid electrostatographic developing apparatus, that is to say, at temperatures up to as high as 125° F.

Satisfactory results are obtained when the total of solid constituents is composed of the four individual solid constituents present in the following ranges of percentages by weight: fixing agent from about 30 to 60 percent, dispersant from about 5 to 30 percent, charge director from about 0.1 to 5 percent, and pigment from about 5 to 40 percent. The fixing agent and dispersant jointly are in excess of 50 percent by weight of the total solid constituents and the charge director and pigment jointly are less than 50 percent.

The following are examples of liquid electrostatographic image developers in concentrated form:

EXAMPLE I

25 gs.	Picco 6120-3
9 gs.	Toner 8100
9 gs.	Spirit Nigrosine SSB
120 gs.	Amsco 460 Solvent
0.25gs.	Aluminum Dresinate
17.5 gs.	50% by weight of a tripolymer of 50 parts by weight of octadecenyl methacrylate, 10 parts by weight of diethyl aminoethyl methacrylate and 40 parts by weight of styrene dissolved in 50% by weight of kerosene

EXAMPLE II

40 gs.	Krumbhaar 484
15 gs.	Toner 8100
15 gs.	Spirit Nigrosine SSB
5 gs.	Raven 11
50 gs.	50% by weight of a tripolymer of 50 parts by weight of octadecenyl methacrylate, 10 parts by weight of diethyl aminoethyl methacrylate and 40 parts by weight of styrene dissolved in 50% by weight of kerosene
150 mls.	Shell Sol 71
2 gs.	Manganese linoleate
2 gs.	Aluminum stearate

EXAMPLE III

25 gs.	Nevchem 100
9 gs.	Toner 8100
9 gs.	Spirit Nigrosine SSB
120 gs.	Shell Sol 71
0.25gs.	Aluminum Dresinate
17.5 gs.	50% by weight of a tripolymer of 50 parts by weight of octadecenyl methacrylate, 10 parts by weight of diethyl aminoethyl methacrylate and 40 parts by weight of styrene dissolved in 50% by weight of kerosene
1 g.	Nopco FOA 2

EXAMPLE IV

55 gs.	Resin NC-11
17.5 gs.	Lube Oil 564
1 g.	Aluminum Stearate
182 gs.	Shell Sol 71
30 gs.	Cadmium Selenide

EXAMPLE V

55 gs.	Resin NC-11
17.5 gs.	50% by weight of a tripolymer of 50 parts by weight of octadecenyl methacrylate, 10 parts by weight of diethyl aminoethyl methacrylate and 40 parts by weight of styrene dissolved in 50% by weight of kerosene
182 gs.	Shell Sol 71
0.5 gs.	Aluminum stearate
28 gs.	Cyan Blue GT 55-3295

Each of the foregoing concentrated liquid electrostatographic developers is formed by introducing all of the recited ingredients into a ball mill and milling the same therein at room temperature for at least 24 hours.

For use in a liquid electrostatographic developing apparatus any one of the concentrated developers of which examples are given above and in which the solid-to-liquid ratio is about one-to-one to about one-to-two are diluted in a ratio of about 2 to 12 grams of concentrated developer to one liter of organic liquid carrier. The original solids concentration is not critical but rather is controlled by economics. The developing concentration depends upon the developing equipment used, the method parameters and the contrast desired so that it is widely variable and is not a critical aspect of the invention. Preferably, when carrying out this dilution the same organic

liquid carrier is used as was employed in the concentrated developer.

Any of said diluted developers can be used in a liquid electrostatographic printing process and will achieve the successful results described at length above. Pursuant to the present invention such developers are used by applying the liquid image developer composition to a latent image consisting of a pattern of electrostatic charges created, for example, in a photoconductive zinc oxide coating applied to a sheet of paper. The liquid developer is applied to such latent image in any well known manner as by spraying or rolling, or by immersing the sheet carrying the image in a receptacle containing the liquid developer. As soon as the image has been developed by electrostatic coupling the sheet is dried, as by subjecting it to an elevated temperature below the char point of the paper, whereupon the liquid carrier will rapidly evaporate and leave a clear image the contrast of which will be controlled only by the developing parameters (time, pigment concentration, etc.).

The said liquid electrostatographic developers in addition to being useful as developers in electrophotography wherein the latent electrostatic image is produced in a photoresponsive medium, such as a zinc oxide or zinc sulfide coating on a surface, also are useful as developers in electrography wherein the latent image is produced in a non-photosensitive dielectric medium on a surface. Moreover said developers can be used in processes wherein the developed image is used as the final image for optical scanning, e.g., reading, or as a copy that is used as a master in a duplicating process, e.g., lithography or offset printing.

It thus will be seen that there are provided liquid electrostatographic image developers which achieve the several objects of the invention and which are well adapted to meet the conditions of practical use.

As various possible embodiments might be made of the above invention and as various changes might be made in the embodiments above set forth, it is to be understood that all matter herein described is to be interpreted as illustrative and not in a limiting sense.

Having thus described the invention, I claim as new and desire to secure by Letters Patent:

1. A liquid electrostatographic image developer for a base sheet having a coating binder for zinc oxide, said developer essentially consisting of a petroleum fraction paraffinic solvent which has less than 2 percent by weight aromatic solvent, a solid film-forming fixing agent dissolved in said solvent, a solid dispersant dissolved in said solvent, a solid charge director carried by said solvent and a sub-micron solid electroscopic pigment material dispersed and insoluble in said solvent, said film-forming fixing agent being present in an amount of about 30 to 60 percent by weight of the solid constituents sufficient to bond to an electrostatographic surface the electroscopic pigment material electrostatically attracted to said surface, said dispersant being present in an amount of about 5 to 30 percent by weight of the solid constituents sufficient to disperse the electroscopic pigment material in the solvent, said charge director being present in an amount of about 0.1 to 5 percent by weight of the solid constituents sufficient to augment the charge direction of the electroscopic pigment material and said electroscopic pigment material being present in an amount of from about 5 percent to about 40 percent by weight of the solid constituents, the film-forming fixing agent and the dispersant being the major proportion of the solid constituents, said solvent having an evaporation rate at least as fast as that of kerosene and slower than that of hexane, a K.B. number of from about 26 to 35, a dielectric constant less than 3½, a flash point of at least 100° F, a viscosity of between 0.5 and 2.5 centipoises at room temperature and being non-toxic, of low odor, of high volume resistivity, nonpolar, substantially aromatic-liquid-free and evaporating rapidly at slighly below the char point of paper, said film-forming fixing agent being non-tacky and tough in solid film form, having a good solvent release and forming a coherent film that bonds well to an electrostatographic surface, all of said solid constituents being mutually compatible and chemically inert to one another at ambient temperatures, the film-forming fixing agent being selected from the group consisting of hydrogenated polymerized wood rosin having an acid number of 145–65 and a softening point of 85° to 93° C by the Hercules drop method, hydrogenated wood rosin having an acid number of 165 and a softening point of 76° C by the Hercules drop method, glycerol ester of modified wood rosin having an acid number of 8 and a softening point of 168° C by the Hercules drop method, pentaerythritol ester of wood rosin having an acid number of 12 and a softening point of 111° C by the Hercules drop method, pentaerythritol ester of polymerized wood rosin having an acid number of 14 and a softening point of 135° C by the Hercules drop method, modified pentaerythritol ester of wood rosin having an acid number of 14 and a softening point of 135° to 159° C by the Hercules drop method, pentaerythritol ester of hydrogenated wood rosin having an acid number of 13 and a softening point of 104° C by the Hercules drop method, pentaerythritol ester of dimeric resin acids having an acid number of 14–15 and a softening point of 159° to 172° C by the Hercules drop method, glycerol ester of polymerized wood rosins having an acid number of 6 and a softening point of 112° C by the Hercules drop method, and pentaerythritol ester of modified wood rosin having an acid number of less than 1 and a softening point of 180° to 190° C by the mercury method, the charge director being selected from the class consisting of aluminum stearate, aluminum dresinate, vanadium dresinate, tin dresinate, cobalt salt to 2-ethyl hexoic acid, iron salt of 2-ethyl hexoic acid, manganese salt of 2-ethyl hexoic acid, manganese linoleate, 1-[2-hydroxyethyl]-2-[mixed pentadecyl and heptacecyl]-2-imidazoline, and a fatty amide condensate and the dispersant being selected from the group consisting of a tripolymer of a weight mixture of 50 parts of octadecenyl methacrylate, 10 parts diethyl aminoethyl methacrylate, and 40 parts styrene, methacrylate polymer, alkyl methacrylate maleic anhydride polymer, maleimide polymer, a polymer consisting of the reaction product of alkyl methacrylate, polyethylene glycol methacrylate and maleic anhydride, a polymer consisting of the reaction product of alkyl methacrylate, polyethylene glycol methacrylate and imide of maleic anhydride and tetraethylene pentamine, polyglycol substituted polyesters and polyglycol substituted polyamides, all said film-forming fixing agents being fully soluble in said solvent.

2. A liquid electrostatographic image developer as set forth in claim 1 wherein the flash point is from about 120° to 152° F.

3. A liquid electrostatographic image developer as set forth in claim 1 wherein the solvent has an IBP of about 345° to 375° F, a dry end point of about 371° to 482° F and an aniline point of about 146° to 187° F.

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