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3,788,995

LIQUID ELECTROGRAPHIC DEVELOPERS

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19 Claims

ABSTRACT OF THE DISCLOSURE

Liquid developers for electrography are made using addition polymers containing a polar moiety and at least one additional moiety having predetermined solubility characteristics with respect to the carrier liquid. Mixtures of these polymers may also be used.

This invention relates to electrography and more particularly to novel liquid developer compositions and their use in the development of electrostatic charge patterns.

Electrophotographic imaging processes and techniques are based on the discovery that certain materials which are normally insulating become conductive during exposure to electromagnetic radiation of certain wavelengths after being electrically charged. Such materials, which may be either organic or inorganic, are termed photoconductors. They are conveniently formed into useable image-forming elements by coating a layer of the photoconductive composition, together with an electrically insulating resinous binder where necessary or desirable, onto a suitable support. Such an element will accept and retain an electrostatic charge in the absence of actinic radiation. In use, the surface of the element is uniformly charged in the dark, typically by placing it under an ion source, such as a corona charger, and exposed to an imagewise pattern of actinic radiation, which selectively reduces the potential of the surface charge to produce a charge pattern corresponding to the radiation pattern. The resultant charge pattern or electrostatic latent image may be developed by contacting it with suitably charged marking particles which adhere in accordance with the charge pattern or it may be transferred to another insulating surface upon which it is developed. The marking particles can be in the form of a dust, i.e., powder, or a pigment in a resinous carrier, i.e., toner, as described, for example, in Giaimo, U.S. Pat. 2,786,440, dated Mar. 26, 1957. The particles may be used or fixed to the surface by known means such as heat or solvent vapor, or they may be transferred to another surface to which they may similarly be fixed, to produce a permanent reproduction of the original radiation pattern.

Dry development systems suffer from the disadvantage that distribution of the powder on the surface of the element is difficult to control. They can have the further disadvantages that excessive amounts of dust may be generated and that high resolution is difficult to attain due to the generally relatively large size of the powder particles. Many of these disadvantages are avoided by the use of a liquid developer of the type described, for example, in Metcalfe et al., U.S. Pat. 2,907,674, issued Oct. 6, 1959. Such developers usually comprise an electrically insulating liquid which serves as a carrier and which contains a dispersion of charged particles comprising a pigment such as carbon black, generally associated with a resinous binder such as, for example, an alkyd resin. A charge control agent is often included in order to stabilize the magnitude and polarity of the charge on the dispersed particles. In some cases, the binder itself serves as a charge control agent.

Many resins used in prior art liquid developers are derived from naturally occurring fats and oils such as soybean oil, linseed oil, and the like. As a consequence, such developers may have a highly variable initial composition. Furthermore, since these natural products typically contain oxidizable or polymerizable groups, developer compositions prepared therefrom are subject to unpredictable change, and the developer is frequently useable for only a very short period of time after preparation. Replenishment of such an aged developer gives inconsistent and unreliable results.

Liquid developers are also frequently used in toner transfer systems. When so used, they must give consistently high uniform density not only on the element on which the image is initially formed but also on the transfer or receiver sheet. Liquid developers of the prior art, including some made with styrene and acrylic esters such as alkyl esters of acrylic and methacrylic acids and their derivatives such as amine derivatives, do not meet the transfer requirement, as image transfer to the receiver sheet is typically spotty, nonuniform and subject to variation with developer age. Developers showing such uncontrollable and unpredictable variations in developed and transferred density do not meet the requirements for stability and consistency demanded in a high volume electrophotographic process.

Accordingly, there is a need in the art for binders for liquid developer compositions which are chemically well characterized and which are not subject to aerial oxidation. There is a further need for liquid developer compositions which can be made reproducibly and which retain their properties for extended periods after preparation.

It is, therefore, an object of this invention to provide novel compositions for the liquid development of electrostatic charge patterns.

It is another object of this invention to provide new, stable liquid developer compositions which retain their charge and dispersion stability for extended periods, and which do not deteriorate with age or upon exposure to the atmosphere.

It is yet another object of this invention to provide liquid developer compositions which are readily replenished after becoming depleted with use.

It is still another object of this invention to provide reproducible liquid electrophotographic developers containing well characterized synthetic resin constituents.

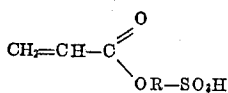
It is a further object of this invention to provide a process for the development of electrostatic charge patterns using the novel liquid developer compositions of this invention.

These and other objects and advantages are accomplished in accordance with this invention by the preparation and use of liquid developer compositions containing certain random copolymers. The term copolymer as used herein has reference to an addition polymer containing at least two randomly recurring monomeric units. The term thus encompasses polymers containing three, four, or occasionally even more randomly recurring monomeric units. The copolymers are more particularly characterized in that they contain as component groups units derived from monomers each of which bears a predetermined relationship to the carrier liquid with which the liquid developer is ultimately prepared. At least one of the monomeric moieties of the copolymer is a polar moiety and at least one other of the monomeric moieties of the copolymer is a moiety soluble in the carrier liquid. The soluble moiety is present in an amount sufficient to yield a dispersibility ratio for the copolymer in the liquid carrier greater than about 0.825. The polar moiety is present in an amount of at least about 1.5×10^{-4} moles/gm. of

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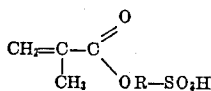
polymer. The polar moiety is a moiety selected from the following group:

(a) Sulfoalkyl acrylates such as compounds having the formula:



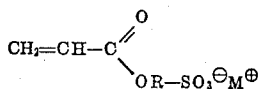
where R is an alkylene group;

(b) Sulfoalkyl methacrylates such as compounds having the formula:



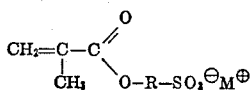
where R is an alkylene group;

(c) Metal salts of sulfoalkyl acrylates such as compounds having the formula:



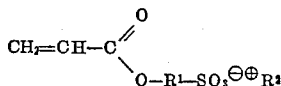
where R is an alkylene group and M^{\oplus} is a metal cation;

(d) Metal salts of sulfoalkyl methacrylates such as compounds having the formula:



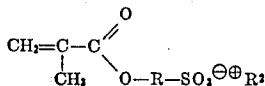
where R is an alkylene group and M^{\oplus} is a metallic cation;

(e) Amine salts of sulfoalkyl acrylates such as compounds having the formula:



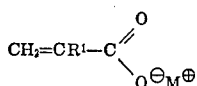
where R^1 is an alkylene group and $\text{R}^2{\oplus}$ is a cation formed from an amine;

(f) Amine salts of sulfoalkyl methacrylate such as compounds having the formula:



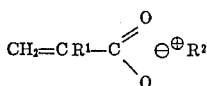
where R is an alkylene group and $\text{R}^2{\oplus}$ is a cation formed from an amine;

(g) Metal salts of acrylic and methacrylic acids such as compounds having the formula:



where R^1 is H or methyl and M^{\oplus} is a metallic cation; and

(h) Amine salts of acrylic and methacrylic acid such as compounds having the formula:



where R^1 is H or methyl and $\text{R}^2{\oplus}$ is a cation formed from an amine; and mixtures thereof.

As used in the present specification the dispersibility ratio of a particular copolymer in a particular developer carrier liquid is defined by the following test. A 4.0 gram quantity of copolymer to be tested is admixed into one liter of a particular developer carrier liquid using a Waring or Polytron Blender operating within the range of 10,000 to 18,000 r.p.m. This mixture is then centrifuged at 34,000 G forces for about 60 minutes. At the end of this time, the mixture is analyzed to determine the amount of polymer which has precipitated. To form the stable

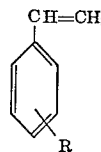
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developers of the present invention, it has been determined that useful polymers should be dispersible to the extent that at least about 3.3 grams of the original 4.0 grams quantity of polymer remain suspended or dissolved in the carrier liquid after centrifuging. The dispersibility ratio is then calculated as the amount of polymer which remains suspended in the carrier liquid divided by the 4.0 grams of polymer originally mixed into the carrier liquid. A dispersibility ratio of 0.825 is equivalent to 3.3 divided by 4.0.

As used in the present specification, "soluble" monomeric moieties which can be copolymerized with the polar moieties to form the copolymers used in the liquid developer of the invention are generally those moieties which, when polymerized, are capable of forming a homopolymer having an inherent viscosity as hereinafter defined of from about 0.4 to about 0.5 in chloroform at room temperature (about 25° C.) and a solubility (at 25° C.) in the carrier liquid to the extent that at least 5 parts by weight of polymer are soluble in 95 parts by weight of carrier liquid. In contrast, the term "insoluble" has reference to a monomeric moiety, a homopolymer of which, under the same conditions, is soluble in the carrier liquid to the extent of less than about 1 part by weight of polymer per 99 parts by weight of carrier liquid.

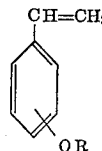
Representative soluble moieties which generally can be copolymerized with the polar moieties set forth to form the copolymers used in the liquid developers of the invention may be selected from the group comprising of:

(a) Alkyl styrenes such as compounds having the formula



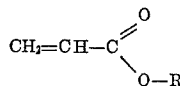
where R is an alkyl having from about 3 to about 10 carbon atoms in the alkyl moiety;

(b) Alkoxy styrenes such as compounds having the formula



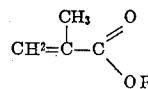
where R is an alkyl having from about 3 to about 10 carbon atoms in the alkyl moiety, for example, p-amyloxy-styrene;

(c) Alkyl acrylates such as compounds having the formula



where R is an alkyl having from about 8 to about 22 carbon atoms in the alkyl moiety;

(d) Alkyl methacrylates such as compounds having the formula



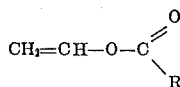
where R is an alkyl having from about 8 to about 22 carbon atoms in the alkyl moiety;

(e) Vinyl alkyl ethers such as compounds having the formula



where R is an alkyl having from about 8 to about 22 carbon atoms in the alkyl moiety; and

(f) Vinyl esters of aliphatic acids such as compounds having the formula:



where R is an alkyl having from about 6 to about 22 carbon atoms in the alkyl moiety; and mixtures thereof.

Other soluble moieties may also be used. Generally, it has been found that if the soluble moiety is present in the copolymer to the extent of at least about 35 weight percent of the polymer, a copolymer is obtained capable of forming a substantially stable dispersion in a typical carrier liquid. Generally, the polar moiety is present in an amount not in excess of about 20 weight percent of the polymer. If no further monomer moiety is present, then, it is preferred that the soluble moiety be present to the extent of at least about 84 weight percent of the polymer.

Preferred polar moieties contained in the copolymers used in the preparation of the liquid developers of the invention generally include the following groups:

Group A.—sulfoalkyl acrylates and sulfoalkyl methacrylates having from 1 to about 4 carbon atoms in the alkyl moiety thereof;

Group B.—metal salts of sulfoalkyl acrylates and sulfoalkyl methacrylates having from 1 to about 4 carbon atoms in the alkyl moiety thereof, the metals forming the metal salts being generally those from Groups I, IIa, IIb and VIII of the Periodic Chart;

Group C.—amine salts of the said sulfoalkyl acrylates and sulfoalkyl methacrylates, and

Group D.—metal salts and amine salts of acrylic and methacrylic acids, the metals forming the metal salts being generally those from the above-noted groups of the Periodic Chart;

and mixtures thereof. Partial metal and amine salts of the ester and acids can also be used, as can mixtures of the complete or partial salts with the salt-free form of the esters and acids. Typical polar groups representative of Groups A-D set forth hereinabove which can be used in the preparation of the copolymers comprising the liquid developers of the present invention include the following:

GROUP A

Sulfoethyl methacrylate
Sulfoethyl acrylate
Sulfopropyl methacrylate
Sulfobutyl methacrylate

GROUP B

Sulfoethyl methacrylate, sodium salt
Sulfoethyl methacrylate, partial sodium salt
Sulfopropyl methacrylate, sodium salt
Sulfobutyl methacrylate, potassium salt
Sulfoethyl methacrylate, lithium salt
Sulfoethyl methacrylate, copper salt

GROUP C

Sulfopropyl methacrylate, dimethylammonium salt
Sulfoethyl methacrylate, diethylammonium salt
Sulfomethyl acrylate, dimethylammonium salt

GROUP D

Sodium methacrylate
Sodium acrylate
Lithium methacrylate
Potassium acrylate
Barium methacrylate
Zinc methacrylate
Cobalt methacrylate
Ferrous acrylate

Magnesium methacrylate
Zinc acrylate

and mixtures thereof.

Preferred soluble moieties contained in the copolymers used in the preparation of the liquid developers of the invention generally include the following:

(a) Alkyl styrenes having from about 5 to about 10 carbon atoms in the alkyl moiety;

(b) Alkyl acrylates and methacrylates having from about 12 to about 22 carbon atoms in the alkyl moiety; and

(c) Vinyl esters of aliphatic acids having from about 10 to about 22 carbon atoms in the alkyl moiety; and mixtures thereof. Typical soluble moieties or groups which can be so used include the following:

4-pentyl styrene
4-hexyl styrene
4-octyl styrene
Lauryl acrylate
Hexadecyl methacrylate
Octadecyl methacrylate
Eicosyl acrylate
Docosyl methacrylate
Vinyl caprate
Vinyl laurate
Vinyl palmitate
Vinyl stearate
Vinyl eicosate
Vinyl docosate

and mixtures thereof.

The term "inherent viscosity," as used herein, is defined by the following formula:

$$\eta_{\text{I}} = l n = \frac{\eta_{\text{solution}}}{\eta_{\text{solvent}}} / C.$$

wherein η_{solution} is the viscosity of the solution, η_{solvent} is the viscosity of the solvent and C is the concentration in grams per 100 ml. of the polymer solvent. The determination is made at a concentration of 0.25 grams of polymer in 100 ml. of chloroform at a temperature of 25° C.

Preferred copolymers used in the preparation of the liquid developers of the invention also contain at least one insoluble moiety or group copolymerized with the aforementioned polar and soluble moieties. Representative insoluble moieties which may be suitable for being so copolymerized include the following:

(a) Styrenes selected from the group of styrene, methyl styrene, methoxy styrene and a halogenated styrene;

(b) Alkyl acrylates having from about 1 to about 4 carbon atoms in the alkyl moiety;

(c) Alkyl methacrylates having from 1 to about 4 carbon atoms in the alkyl moiety;

(d) Vinyl alkyl ethers having from 1 to about 4 carbon atoms in the alkyl moiety; and

(e) Vinyl esters of aliphatic acids having from about 1 to about 4 carbon atoms in the alkyl moiety; and mixtures thereof.

Preferred insoluble moieties contained in the copolymers used in the preparation of the subject liquid developers generally include the following:

(a) Styrene and methyl styrene;

(b) Alkyl acrylates having from 1 to about 4 carbon atoms in the alkyl moiety;

(c) Alkyl methacrylates having from 1 to about 4 carbon atoms in the alkyl moiety; and

(d) Vinyl esters of aliphatic acids having from 1 to about 4 carbon atoms in the alkyl moiety; and mixtures thereof. Typical insoluble moieties or groups which can be so used include the following:

Styrene
 α -Methyl styrene
Ethyl acrylate

Methyl acrylate
 Butyl acrylate
 Ethyl methacrylate
 Propyl methacrylate
 Butyl methacrylate
 Vinyl acetate
 Vinyl propionate
 Vinyl butyrate

and mixtures thereof.

It will be apparent that the choice of particular soluble, insoluble and polar monomeric moieties is determined by a number of factors. The degree of solubility in the carrier liquid may be controlled by proper adjustment of the ratio of soluble moiety to insoluble moiety. In addition, the nature of the particular soluble monomeric moiety, such as the degree of solubility of a homopolymer comprising it, will influence the particular insoluble monomeric moiety chosen to copolymerize with it to give the final polymer. For example, if the soluble monomer is one having a relatively long alkyl group attached to it, rendering a polymer containing it relatively soluble, the insoluble monomer is desirably one having a relatively short alkyl group attached to it, to balance the properties. On the other hand, a relatively short alkyl group on the soluble monomer in general requires a somewhat longer alkyl group on the insoluble monomer. Generally, as indicated above, useful polymers of the present invention are dispersible in the carrier liquid to the extent that if a 4.0 gram quantity of polymer is added to one liter of carrier, at least about 3.3 grams will remain dispersed therein after centrifuging the mixture at 34,000 G forces for about 60 minutes.

In general, the polymers comprising the liquid developers of the invention are prepared by an addition polymerization reaction wherein all of the component monomers are combined in a reaction vessel in a reaction medium, such as dioxane, and a suitable free radical initiator. The vessel containing the solution is then flushed with an inert gas, such as nitrogen, and heated to a temperature sufficient for the polymerization reaction to proceed at a reasonable rate. The temperature, in general, is above room temperature and preferably about 40 to 80° C. After the polymer has formed, it is removed from the reaction mixture and purified as necessary. Polymers produced according to this procedure typically have an inherent viscosity, as hereinbefore defined and measured, in the range of from about 0.1 to about 0.8. The resultant polymers contain recurring units of one or more moieties derived from soluble monomers, one or more moieties derived from insoluble monomers, and one or more moieties derived from polar monomers. In general, a typical polymer used in the liquid developers of the invention contains from about 35 to about 70 weight percent of soluble moieties, from about 30 to about 65 weight percent of insoluble moieties and from about 1.5 to about 20 weight percent of polar moieties. Preferred polymers of the invention contain from about 40-55 weight percent soluble moiety, from about 35-55 weight percent of insoluble moiety and from 1.5-16 percent polar moiety. The dispersibility of the polymer can be adjusted as desired by proper balancing of the relative abundance of the soluble and insoluble moieties. The relative amount of polar moiety can be varied to provide polymers having different charge properties when incorporated into a liquid developer. Mechanical properties such as abrasion resistance, and fixability of the resultant toner image can also be adjusted at will by properly balancing the ratio of the components in the polymer.

It should be noted that the relative abundance of the various starting monomers in the polymerization medium is not always indicative of the percentage composition to be expected in the resultant polymer. When acrylic monomers are used as starting materials, for example, it is found that the composition of the polymer bears a very close correlation to the relative abundance in the starting

solution, whereas when styrenes are used as starting materials, the correlation is not so close. Such deviations are well known to the polymer chemist, and one skilled in the art should readily be able to produce such variations in composition as may be desired to meet particular requirements.

As has been mentioned, a wide variety of salts of the polymers can be used. Useful salts include those of metals chosen from Groups I, IIa, IIb and VIII of the Periodic Chart of the Elements (see, for example Handbook of Chemistry and Physics, 51st edition, 1970-1971, p. B-3). Preferred salts are those of lithium, sodium, potassium, copper, magnesium, barium, calcium, zinc, cadmium, iron, and cobalt, with those of lithium, sodium, potassium, copper, barium, zinc and cobalt being particularly preferred. The salts may be complete or partial salts of the polymer, and may be made by any of several procedures. As an example, a polymer containing the desired moieties may be made first and converted to the salt form by mixing with a suitable metal compound in the proper reaction medium. Useful compounds for this purpose are, for example, the hydroxides or carbonates of the metal. Alternatively, the appropriate monomer may be converted to the salt form before polymerization, by treating it with a base or basic salt of the metal, followed by polymerization of the salt form into the desired polymer. Partial salts can also be formed by using as starting materials a blend of converted and unconverted monomers in the polymerization medium. The proportion of the salt form present is determined by the relative quantities of the two forms present when polymerization is initiated.

Liquid developers containing the novel polymers described herein typically comprise a dispersion of the polymer in a suitable carrier liquid. A common method of preparing such a dispersion is solvent milling. A quantity of the polymer is dissolved in a suitable solvent and the solution placed in a ball mill. Pigments and other additives which may be necessary or desirable are added to the mix and the whole milled for a suitable time, typically up to a week. Alternatively, a viscous solution of the polymer is placed on compounding rolls having chilled (5 to 10° C.) water passing through the cooling system. Pigments and other additives are then placed on the rolls and thoroughly mixed and blended with the polymer. The pigment is generally present in an amount of from about 200 to about 10 percent of the weight of the resin. After passing the complete mix through the mill several times to completely blend the ingredients, the mix is removed.

Liquid developers are made from the toner concentrate formed as above by dispersing the concentrate in a suitable electrically insulating carrier liquid. Carrier liquids which may be used to form such developers can be selected from a wide variety of materials. Preferably, the liquid has a low dielectric constant and a very high electrical resistance such that it will not disturb or destroy the electrostatic charge pattern being developed. In general, useful carrier liquids should have a dielectric constant of less than about 3, should have a volume resistivity greater than about 10¹⁰ ohm-cm. and should be stable under a variety of conditions. Suitable carrier liquids include halogenated hydrocarbon solvents, for example, fluorinated lower alkanes, such as trichloromonofluoromethane, trichlorotrifluoroethane, etc., having a boiling range typically from about 2° C. to about 55° C. Other hydrocarbon solvents are useful, such as isoparaffinic hydrocarbons having a boiling range of from about 145° C. to about 185° C., such as Isopar G (Humble Oil and Refining Co.) or cyclohydrocarbons such as cyclohexane. Additional carrier liquids which may be useful in certain situations include polysiloxanes, odorless mineral spirits, octane, etc.

Although it is possible to use the resinous copolymers to prepare liquid developers without further addenda, as in situations in which a colorless image is desired, it is customary to add a colorant to give the image optical

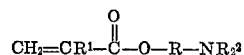
density. Useful colorants can be selected from a variety of materials such as dyestuffs or pigments. Virtually any of the compounds mentioned in the Color Index, second edition, 1956, vols. I and II, may, in principle, be used. Included among the vast number of useful colorants would be such materials as Hansa Yellow G (C.I. 11680), Nigrosine Spirit soluble (C.I. 50415), Chromogen Black ETOO (C.I. 14645), Rhodamine B (C.I. 45170), Solvent Black 3 (C.I. 26150), Fuchsine N (C.I. 42510), C.I. Basic Blue 9 (C.I. 52015), etc. Another useful class of colorants is comprised of nigrosine salts of mono- and difunctional organic acids having from about 2 to about 20 carbon atoms such as chloroacetic acid, stearic acid, sebacic acid, lauric acid, azelaic acid, adipic acid, abietic acid and the like. Nigrosine salts of this type are disclosed in copending application of Olson, U.S. Ser. No. 770,122, filed Oct. 23, 1968, entitled Uniform Polarity Resin Electrostatic Toners now Pat. No. 3,647,696 issued Mar. 7, 1972.

Other colorants suitable for use in preparing liquid developers from the polymers described herein include salts of water-soluble acid dyes, more particularly the metal, alkali metal and ammonium salts of dyes having sulfonic and/or carboxylic acid groups contained thereon. Exemplary of these are the lead salt of copper phthalocyanine tetrasulfonic acid and the magnesium salt of 1-(p-sulfophenyl-3-phenyl) - 4 - (2,5-dichloro-4-sulfophenyl-azo)-5-pyrazolone. These colorants are more particularly described in copending application of Chechak, U.S. Ser. No. 864,299, filed Oct. 3, 1969 and now abandoned, entitled Liquid Developer and Method. Particularly useful colorants are pigments prepared from the reaction of a strongly acid dye with a strongly basic dye to form a highly insoluble precipitate having essentially no color dilution. These pigments and their method of preparation are more fully disclosed in copending application of Chechak, U.S. Ser. No. 58,190, filed July 24, 1970 and now abandoned, entitled Novel Pigments and their Preparation and Use.

As has been indicated, the polymers described herein are very useful for preparing liquid developers which are stable and which produce permanent images of high quality. However, under certain image-forming conditions, improved results may be obtained when at least one additional polymer is added to the composition forming a liquid developer. The use of two or more copolymers in this way permits much greater flexibility in the formulation of developers designed especially for toner transfer, for example. Thus, it is found that preparation of liquid developers having the capability of producing an image which cleanly transfers to a receiver sheet to form thereon an image having high uniform density free from background, and which developer is at the same time readily replenishable, is greatly facilitated by the use therein of two or more polymers of the general type herein disclosed. At least one of these polymers (Type A) is of the type and has a composition as already described in detail, while at least one other of these polymers (Type B) may be of the type hereinafter more particularly set forth. The Type B polymer is a copolymer containing at least an insoluble moiety, as hereinbefore defined, which is present in an amount of at least about 55 weight percent of the polymer, and a polar moiety which is present in an amount within the range of 0.5 to 20 weight percent of the polymer. The polar moiety is selected from the group comprising:

- (a) Sulfoalkyl acrylates;
- (b) Sulfoalkyl methacrylates;
- (c) Metal salts of sulfoalkyl acrylates;
- (d) Metal salts of sulfoalkyl methacrylates;
- (e) Amine salts of sulfoalkyl acrylates;
- (f) Amine salts of sulfoalkyl methacrylates;
- (g) Metal salts of acrylic and methacrylic acids;
- (h) Amine salts of acrylic and methacrylic acids;

- (i) Acrylic and methacrylic acids;
- (j) Amino substituted alkyl methacrylates and acrylates such as compounds having the formula



where R¹ is H or methyl, R is alkylene, and R² is H or alkyl, and mixtures thereof.

Insoluble moieties which can be copolymerized with the polar moiety or moieties are generally those from the same group indicated hereinbefore with reference to the Type A copolymer. Although it has been indicated that the amount of insoluble monomer is at least about 55 weight percent of the Type B polymer, best results are obtained if the polar moiety is present in an amount of not in excess of about 16 weight percent of the polymer. Thus, if no further monomeric moiety is present, it is preferred that the insoluble moiety be present to the extent of at least about 84 weight percent of the polymer.

Preferred polar moieties contained in said Type B polymer generally include the following:

(A) sulfoalkyl acrylates and sulfoalkyl methacrylates having from 1 to about 4 carbon atoms in the alkyl moiety thereof;

(B) metal salts of sulfoalkyl acrylates and sulfoalkyl methacrylates having from 1 to about 4 carbon atoms in the alkyl moiety thereof, the metals forming the metal salts being generally those from Groups I, IIa, IIb and VIII of the Periodic Chart;

(C) amine salts of the said sulfoalkyl acrylates and sulfoalkyl methacrylates, including substituted amine salts;

(D) metal salts and amine salts of acrylic and methacrylic acids, the metals forming the metal salts being generally those from the above-noted groups of the Periodic Chart;

(E) aminoalkyl methacrylates and acrylates having from 1 to about 4 carbon atoms in the alkyl moiety thereof, preferred amino groups including an alkylamino group having from 1 to about 4 carbon atoms in the alkyl moiety thereof including a dialkylamino group;

(F) acrylic and methacrylic acids; and mixtures thereof.

The polar group of the Type B polymer can also comprise partial metal salts and partial amine salts of the esters and acids and mixtures thereof with each other and with free form of the esters and acids. Typical polar groups which can be used include all those set forth as suitable for the Type A polymer and, in addition, groups such as those set forth hereinafter:

Acrylic acid
 Methacrylic acid
 Diethylaminoethyl methacrylate
 Dimethylaminoethyl methacrylate
 Ethylpropylaminoethyl acrylate
 Dibutylaminoethyl methacrylate
 Diethylaminobutyl acrylate
 Dibutylaminoethyl acrylate

Preferred copolymers used as the Type B polymer in the liquid developers of the invention also contain at least one soluble moiety or group copolymerized with the aforementioned polar and insoluble moieties. Suitable soluble moieties are selected from the group generally as those which are suitable for incorporation in the Type A copolymer. When a copolymer containing at least three monomeric moieties of the types described is prepared for use as the Type B polymer, it is preferred that the polar moiety be present in an amount of from about 0.5 to about 16 weight percent, the insoluble moiety be present in an amount of from about 60 to 85 weight percent, and the soluble moiety be present in an amount of from about 10 to about 25 weight percent. If more than three distinct monomeric entities are included in the polymer, the above weight composition applies generally to the type of moiety

involved and not necessarily to the presence of a distinct chemical species. As is evident, wide variations in composition within these broad ranges may be made to adapt developer compositions to meet the requirements of particular situations.

A number of advantages are realized through the use of two or more polymers of the type described in the liquid developer compositions of the invention. These advantages relate to density control, transfer characteristics and replenishment. These three properties are particularly important in those situations in which the developers are to be used in preparing images in a three-color transfer process.

Density control refers to a property desirable in multi-color reproduction processes in which separate color images are superimposed to produce a copy of an original. In such processes each transferred image to be superposed should bear a predetermined tonal relationship to the original from which it is derived. To a certain extent, the tonal relationships can be controlled by electrical parameters, such as the relationship connecting surface potential of the photoconductive element used to produce the image and the exposure received by the element, that is, the "electrical H and D" curve. The translation of this electrical curve into the corresponding visual curve, however, is controlled predominantly by the charge characteristics of the toner particles. Developers in which density is not sensitive to changes in binder-to-pigment ratio or to changes in polar group concentration are considered, for purposes of this invention, to have poor density control, while developers in which density is quite sensitive to these parameters are considered to have good density control.

Another aspect of the preparation of multiple-use developers involves their transfer characteristics. In transfer processes such as the above, it is desirable that each colored image transfer substantially completely, thereby duplicating consistently on the receiver member the tonal scale that is developed on the photoconductive element. Developers that give images which transfer completely and therefore duplicate the developed tone scale are considered, for purposes of this invention, to have good transfer characteristics. Developers which give images which transfer only partially or which do not duplicate the tone scale on the element are considered to have poor transfer characteristics.

A further aspect of the preparation of developers for multiple use involves replenishment. In such processes, it is desirable that the composition of the developer remain essentially constant with use and that the reproduction quality of many successive transferred images is not affected by such use. To prevent change in transfer reproduction characteristics, the developer components removed must be replenished at regular intervals. If the various components, such as binder, pigment, etc., deposit on the image in such proportions that they can be satisfactorily replenished in the remaining developer, the developer is considered to have good replenishment characteristics for the purposes of this invention. If, however, they deposit on the image in such proportions that they cannot be replenished totally, the developer is considered to have poor replenishment characteristics.

Developers containing a mixture of at least two polymers of the types herein described are found to have unexpectedly enhanced characteristics. The resultant developers are stable and well dispersed, have excellent replenishment characteristics, produce images having excellent density control, and yield complete and uniform transfer. The advantage of such a mixed polymer developer over a developer containing only a Type A polymer relates principally to the transfer and replenishment aspects of multiple use. A mixed polymer developer shows greatly improved performance in these respects over a developer containing only a Type A polymer. A

developer containing only a Type B polymer, on the other hand, either will not disperse or has poor replenishment characteristics and yields images having poor density control. Both types of single-polymer developers yield images which do not transfer cleanly and completely; however, this is not a problem in those situations where transfer is not necessary. In such situations, that is, in cases in which the toner image is produced directly on the element which will bear the final image, uniform and complete transfer is obviously not a requirement to be met.

Polymers of the two types described hereinbefore may be combined over a wide range of weight ratios. In general, the weight ratio of the two polymers is determined by several factors including the optical density desired or the quantity of polymer to be deposited for a given charge level, the physical and transfer properties of the image and developer stability. Charge per particle is, in general, controlled by the total quantity of polar groups present in both polymers. The less polar group present, the higher the density or quantity of polymer deposited per given charge level. If high densities are desired, it is generally desirable to use polymers with a relatively small number of polar groups; or, if one of the polymers utilized contains a relatively high level of polar groups, then the other polymer(s) should contain a low level of polar groups. In the case where low densities are desired, it is usually desirable to use a relatively high level of polar groups in both polymers; or, if the level of polar groups in one of the polymers utilized is relatively low, then the level of polar groups in the other polymer(s) should be relatively high. Similarly, the relative abundance of soluble and insoluble moieties contained in the Type A and Type B polymers can be varied to obtain the optimum balance between the various properties desired. Generally, the weight ratio of Type B polymer to Type A polymer may be varied between 0.1 to 3, preferably between 0.25 to 1.5. If a pigment is used, in general, the Type B polymer is present in an amount of from about 0.2 to about 2.5 times the weight of the pigment, with from about 0.5 to 2.0 being preferred. The Type A polymer may be present in an amount of from about 0.1 to about 5.0 times the weight of the pigment, with from about 0.3 to about 2.5 being preferred.

Developer concentrates containing two or more polymers of the types described herein are usually prepared by initially dissolving the Type B polymer in a suitable solvent and milling the solution with the pigment for a suitable period of time. Alternatively, however, developers can be prepared by milling the pigment into the Type A polymer and later adding a solution of the Type B polymer, or the pigments can be milled in mixtures of two or more polymers. In the case where no pigment is used, Type A and Type B polymers are usually dissolved separately, combined in the desired proportions and then dispersed in the carrier liquid. The time is determined by the amount of milling required to reduce the pigment particle size to less than one micron, preferably 0.1 to 0.2 micron. Typical times range up to ten days. A predetermined portion of the dispersion thus obtained is combined with a solution of the Type A polymer, and the mixed resin dispersion mixed or milled for a period of time ranging typically from one-half hour to an hour to ensure complete and uniform blending. Alternatively, in the case of both pigmented and unpigmented concentrates, it is sometimes preferable to dilute the concentrates with approximately an equal volume of carrier liquid before dispersion of the concentrates in the liquid carrier to form the working developer.

Because the developers of this invention have a unique combination of charge and solubility properties, they generally do not require addition of compounds such as cobalt naphthenate and the like to supplement the charge conferred by the polymers themselves. In general, a single polymer of the type described herein or at least a mixture

of that polymer with another provides adequate charge and stability.

The amount of polymer used in the developer of the present invention may vary within a fairly wide range. Typically, there is present an amount of polymer within the range of from about 0.01 to about 15 percent by weight of the total developer composition. The carrier liquid represents the bulk of the developer; typically from about 85 to about 99 percent by weight of the developer comprises the carrier liquid, typically 93 to about 99 percent of developer comprises the carrier liquid.

The following examples are included for a further understanding of the invention:

Example 1.—Preparation of poly(styrene-co-lauryl methacrylate-co-2-sulfoethyl methacrylate)

The following materials are dissolved in 25 ml. of 1,4-dioxane:

	G.
Styrene -----	25
Lauryl methacrylate -----	23
2-sulfoethyl methacrylate -----	2
Azoisobutyronitrile -----	0.4

The solution is flushed with nitrogen and heated at 60° C. for 24 hours. The polymer is precipitated by pouring the mixture into water. The liquid is decanted from the soft product, and the polymer washed by allowing it to stand in fresh water for several hours. The water is poured off, and the product dried in vacuum at 40° C. There is obtained a 45 gram quantity of product having an inherent viscosity in chloroform of 0.32.

Example 2.—Preparation of poly(styrene-co-lauryl methacrylate-co-sodium acrylate)

The procedure of Example 1 is followed with the exception that 4 grams of acrylic acid is substituted for the sulfoethyl methacrylic in the first step. After washing and drying, there results 45 g. of the free acid form of the polymer, which has an inherent viscosity of 0.29. A 10.5 g. portion of this polymer, dissolved in 200 ml. of chloroform, is shaken well with 0.48 g. of sodium carbonate dissolved in 25 ml. of water, forming an emulsion. Stirring the mixture into isopropanol precipitates the sodium salt form of the polymer. It is washed in water and vacuum dried as in Example 1.

Example 3.—Preparation of poly(styrene-co-lauryl methacrylate-co-3-sulfoethyl methacrylate, sodium salt)

A one-liter polymerization flask fitted with a mechanical stirrer and a nitrogen inlet tube is charged with 125 g. of styrene, 115 g. of lauryl methacrylate, 10 g. of methacrylic acid, 125 g. of 1,4-dioxane and 1.25 g. of 2,2'-azobis(2-methylpropionitrile). Nitrogen gas is bubbled through the mixture for several minutes, then the mixture is heated with stirring for 16 hours at 70° C. To the clear, colorless dope resulting is added 50 ml. of a 16 weight percent aqueous sodium hydroxide solution, while stirring is continued at 75° C. for 10 minutes. To the solution containing poly(styrene-lauryl methacrylate-methacrylic acid, sodium salt) is then added 20 ml. of 1,3-propane sultone with stirring at 75° C. for one hour. To the thickened dope is added 125 ml. of 1,4-dioxane, and stirring continued at a temperature of 80° C. The white emulsified dope is poured into 3 l. of hot tap water. The polymerization flask is then rinsed with 125 ml. of dioxane, which is poured into the water. The polymer is kneaded, the water drained, the polymer kneaded again in hot tap water, separated, kneaded twice in cold tap water, separated and dried for 16 hours at 80° C. under vacuum. There results a 245.5 g. yield of white solid having an inherent viscosity of 0.28. Alternatively, the sodium salt form of the polymer may be prepared by first forming the monomeric sodium sulfoethyl methacrylate and substituting it for the methacrylic acid in the starting solution.

A developer concentrate is prepared by milling in a ball mill a 1 g. portion of the sodium salt of poly(styrene-co-lauryl methacrylate-co-3-sulfoethyl methacrylate), 46:50:4 by weight, with 0.5 g. each of Rhodamine Y (C. I. 45160) and Permanent Cerise T (C. I. 45160) in 30 ml. of Solvesso 100. Solvesso 100 is a cyclohydrocarbon having a major aromatic component and having a boiling range of from about 150 to about 185° C., sold by Humble Oil and Refining Co. A 6 ml. portion of the concentrate is added dropwise to 244 ml. of Isopar G under conditions of high shear. The resultant developer is stable and does not settle upon storage on the shelf for a period of 180 days. When used to develop a negatively charged image on a photoconductive element comprising an organic photoconductor-containing layer carried by a conductive support, the developer produces a good reproduction of the image, having a maximum density of 1.5. A similar developer prepared from a polymer containing dimethylaminoethyl methacrylate in place of the 3-sulfoethyl methacrylate sodium salt does not give the same high density and settles upon standing in a much shorter period of time.

Example 5

A developer concentrate is prepared by milling 1 g. of poly(styrene-co-lauryl methacrylate-co-sulfoethyl methacrylate), 46:50:4 by weight, with 0.5 g. of each of the dyes of Example 4 in 15 ml. of Solvesso 100. After 2 days milling, an additional 15 ml. of Solvesso 100 are added. A developer is prepared as in Example 4, adding 12 ml. of the concentrate to 492 ml. of Isopar G. The stability of the developer is comparable to that of the developer of Example 4. When used to develop an electrostatic charge pattern as in Example 4. The developer gives a faithful reproduction and high density.

Example 6

A developer concentrate is prepared by milling together 1 g. of the sodium salt of poly(styrene-co-lauryl methacrylate-co-acrylic acid), 50:46:4 by weight, with 0.5 g. of each of the colorants of Example 4, in 15 ml. of Solvesso 100, as in the previous examples. After two days of milling, 2 g. of additional polymer and 30 ml. of Solvesso 100 are added to produce a concentrate having a binder:pigment ratio of 3:1. A developer is formed by adding dropwise 10.5 ml. of the concentrate to 240 ml. of Isopar G in a high speed blender which produces high shear, as previously. There results a stable, positively charged developer having particles in the range under 1 to 2 microns in size. When used to produce an image on a charged organic photoconductive element as in the previous examples, the developer yields an image having contrast and having a density to green light of in excess of 2.0. A developer prepared in the identical manner which uses, instead, as the polymer, poly(styrene-co-lauryl methacrylate-co-acrylic acid), as taught by the prior art, is not stable, as the pigments will not disperse in the carrier liquid.

Example 6A

A developer is prepared as in Example 6 except the lithium salt of poly(styrene-co-lauryl methacrylate-co-methacrylic acid) 50:46:4 is used. This developer performs in the same manner as the developer described in Example 6.

Example 6B

A developer is prepared as in Example 6A except the concentrate is milled in 20 ml. of Isopar G. This developer performs in the same manner as the developer described in Example 6.

Example 7

A developer concentrate is prepared by milling together 1 g. of copper phthalocyanine pigment (Monastral Fast Blue B, C. I. 74160, Imperial Chemical Industries, Lt.) and

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1 g. of poly(butyl methacrylate-co-lauryl methacrylate-co-2-sulfoethyl methacrylate), 40:50:10 by weight, in 20 ml. of Solvesso 100. A developer is prepared by dispersing 3.2 g. of the concentrate in 330 ml. of Isopar G in the manner previously described. There results a very stable developer which yields images of high density on a charge-bearing organic photoconductive element. Similar results are obtained by using as the starting monomers ethyl methacrylate and octadecyl methacrylate in place of the butyl methacrylate and lauryl methacrylate, respectively.

Example 8

A developer concentrate is prepared by milling together 1 g. of the sodium salt of poly(styrene-co-lauryl methacrylate-co-methacrylic acid, 46:50:4 by weight and 1 g. of the diazo dye Permanent Yellow HR (C.I. Pigment Yellow 83, Farbwerke Hoechst, AG) in 20 ml. of Solvesso 100. A 3.4 ml. portion of the concentrate is added to 3.4 ml. of Isopar G, shaken for one minute, and the combination added to 326 ml. of Isopar G under conditions of high shear. There results a very stable developer having positive charge with which an electrostatic charge pattern on an organic photoconductive element is developed. The developed image has a maximum density of 2.0. No settling of the developer occurs within six days after preparation. A developer made from a concentrate similarly prepared with the exception that the polymer contains the free acid instead of the sodium salt is also used to develop a charge pattern as above. When used immediately, the developer gives an equivalent maximum density; however, dispersion stability is poor, as the developer settles virtually completely within 24 hours.

Example 9

Concentrate 9 is prepared by milling in a ball mill a 1 g. portion of poly(butyl methacrylate-co-lauryl methacrylate-co-2-sulfoethyl methacrylate, 77:15:8 by weight, 20 ml. of Solvesso 100, and 1 g. of red pigment, the 50:50 phosphotungstic:phosphomolybdic acid salt of C.I. 48070 red dye. Solution 9 is prepared by dissolving 1 g. of poly(styrene-co-lauryl methacrylate - co - 2 - sulfoethyl methacrylate), 38:52:10 by weight, in 20 ml. of Solvesso 100. A liquid developer is made by combining 3.2 g. of Concentrate 9 with 3.4 ml. of Solution 9 using gentle agitation, and adding the mixture dropwise to 326 ml. of Isopar G in a high speed blender. A second liquid developer is made in the same manner, except that the amount of Solution 9 is one-half of that used above. Two identical organic photoconductive compositions are treated as follows: Each is given a uniform positive charge and exposed through a negative original to produce an electrostatic charge pattern of positive polarity such that the unexposed areas have a maximum positive polarity and the exposed areas have a differential positive charge proportional to the exposure. When the two developers made, as described above, are flowed over the respective surfaces of these two photoconductive compositions bearing these charge patterns in the presence of a facing electrode having a positive charge slightly lower than the maximum charge on the organic photoconductor, positive images are produced from negative originals. The density of the images obtained may be varied to an extent by varying the level of charge of the organic photoconductor and facing electrode and by varying the exposure level. Both developed images transfer cleanly to a paper receiving sheet by the application of an electrostatic charge to the rear surface of the paper. The transferred images are clean, free from smudging and of high, uniform density. A developer prepared as above except that Solution 9 and its dissolved resin are omitted agglomerates immediately upon addition to the Isopar G, and no image can be formed therefrom. If concentrate 9 is instead prepared with the second named resin above and a solution containing the first resin only is not added, an image is formed,

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but it does not transfer cleanly to the receiver sheet. A developer prepared as first set forth but with the order of addition of the resins reversed also produces a stable developer which transfers cleanly and completely.

Example 10

Concentrate 10 is prepared as set forth in Example 9 except that the polymer is a 1 g. portion of poly(butyl methacrylate - co - lauryl methacrylate - co - 2-sulfoethyl methacrylate), 77:15:8 by weight, the pigment is copper phthalocyanine tetrasulfonate, cadmium salt, and the solvent is 20 ml. of Solvesso 100. Solution 10 is prepared by dissolving 1 g. of the sodium salt of poly(styrene-co-lauryl methacrylate - co - 3 - sulfopropyl methacrylate), 47:43:10 by weight, in 20 ml. of Solvesso 100. A 3.2 g. portion of Concentrate 10 and a 3.4 ml. portion of Solution 10 are gently mixed together and added dropwise to 3.4 ml. of Isopar G, to produce a liquid developer. A second liquid developer is made in the same manner, except that the amount of Solution 10 is one-half of that set forth above. When used to develop an electrostatic charge pattern as in Example 9, a dense blue image is obtained, which transfers completely and uniformly to a transfer sheet. A developer prepared by omitting Solution 10 from the mixture agglomerates upon addition of the Isopar.

Example 11

A 1 g. portion of poly(butyl methacrylate-co-lauryl methacrylate-co-sulfoethyl methacrylate), 80:16:4 by weight, is dissolved in 20 ml. of Solvesso 100, and 0.25 g. of copper acetate added to the mill and the whole milled for 8 hours to convert the polymer to the copper salt. A 1 g. portion of the pigment of Example 9 is next added to the mill, and milling continued for 64 hours. A 3.2 g. portion of Concentrate 11 thus formed is mixed with 3.4 ml. of Solution 10 of Example 10 using gentle agitation, and the combination added dropwise to 326 ml. of Isopar G to form a liquid developer. An electrostatic charge pattern developed with this developer yields a high density image having good density control. The image transfers uniformly and completely to a transfer sheet when transfer is carried out as in the previous examples.

Example 12

Concentrate 12 is prepared by milling in a ball mill a 1 g. portion of poly(butyl methacrylate-co-ethyl methacrylate-co-lauryl methacrylate-co-2-sulfoethyl methacrylate), 26:50:16:8 by weight, 20 ml. of Solvesso 100, and 1 g. of the pigment of Example 7. Solution 12 is prepared by dissolving 0.5 g. of poly(styrene-co-lauryl methacrylate-co-2-sulfoethyl methacrylate), 38:52:10 by weight, in 20 ml. of Solvesso 100, and adding thereto 0.5 g. of its partial sodium salt. A liquid developer is made by gently mixing together a 3.2 g. portion of Concentrate 12 and a 3.4 ml. portion of Solution 12, and adding the mixture dropwise under shearing conditions to 326 ml. of Isopar G. When used to develop an electrostatic charge pattern as in the previous examples, the developer produces a very high density image which transfers uniformly and completely to a paper receiver sheet. A developer made using the resin of Concentrate 12 alone without the resin of Solution 12 agglomerates promptly upon preparation.

Example 13

Concentrate 13 is prepared by milling together in a ball mill a 1 g. portion of poly(ethyl methacrylate-co-lauryl methacrylate - co - 2 - sulfoethyl methacrylate), 76:16:8 by weight, 1 g. of the pigment of Example 7 and 20 ml. of Solvesso 100. Solution 13 is prepared by dissolving 0.5 g. of poly(styrene-co-lauryl methacrylate-co-2-sulfoethyl methacrylate) and 0.5 g. of its partial sodium salt, both 46:46:8 by weight, in 20 ml. of Solvesso 100. A liquid developer is made by combining 3.2 g. of Con-

concentrate 13 with 6.8 ml. of Solution 13, and adding the mixture to 3.23 ml. of Isopar G dropwise, under conditions of high shear. When used to develop an electrostatic charge pattern, the developer produces a high density image which transfers well to a paper receiving sheet. The developer has excellent replenishment characteristics. If the resin of Concentrate 13 is used alone to prepare the liquid developer, and the resin of Solution 13 is not used, the developer is unstable.

Example 14

Concentrate 14 is prepared by milling in a ball mill a 1 g. portion of poly(butyl methacrylate-co-lauryl methacrylate-co-dimethylaminoethyl methacrylate-co-acrylic acid), 78:16:4:2 by weight, 1 g. of the pigment of Example 9 and 20 ml. of Solvesso 100. Solution 14 is prepared by dissolving g. of poly(styrene-co-lauryl methacrylate-co-2-sulfoethyl methacrylate), 38:52:10 by weight, in 20 ml. of Solvesso 100. A liquid developer is made by combining 3.2 g. of Concentrate 14 with 3.4 ml. of Solution 14, and adding the mixture dropwise to 326 ml. of Isopar G under conditions of high shear. When used to develop an electrostatic charge pattern as in the previous examples, the developer gives a high density image and has good density control. When transferred as previously indicated, the image has high, uniform density on the transfer sheet. A developer made using Concentrate 14 alone, in the absence of Solution 14, agglomerates in the mixing container. Similar results are obtained by using 5.1 ml. of the following Solution 14a in place of the 3.4 ml. of Solution 14 and mixing with Concentrate 14 to form the developer Solution 14a contains 1 g. of poly(styrene-co-lauryl methacrylate-co-2-sulfoethyl methacrylate), 46:46:8 by weight dissolved in 20 ml. of Solvesso 100.

Example 15

Concentrate 15 is prepared by milling in a ball mill a 1 g. portion of the lithium salt of poly(butyl methacrylate-co-lauryl methacrylate-co-sulfoethyl methacrylate), 76:16:8 by weight, 1 g. of the pigment of Example 5, and 20 ml. of Solvesso 100. Solution 15 is prepared by dissolving 1 g. of the partial sodium salt of poly(styrene-co-lauryl methacrylate-co-2-sulfoethyl methacrylate), 38:52:10, in 20 ml. of Solvesso 100. A liquid developer is made by combining 3.2 g. of Concentrate 5 with 3.4 ml. of Solution 15, and adding the mixture dropwise as in the previous examples to 326 ml. of Isopar G. The resulting developer has good marking characteristics and good density control. A developer made using Concentrate 15 alone and not containing Solution 15 is not stable and agglomerates very shortly after preparation.

Example 16

Concentrate 16 is prepared by milling in a ball mill a 1 g. portion of poly(ethyl acrylate-co-ethyl methacrylate-co-acrylic acid), 36:30:16:12:6 by weight, 1 g. of the pigment of Example 9, and 20 ml. of Solvesso 100. Solution 16 is prepared by dissolving 1 g. of the lithium salt of poly(styrene-co-lauryl methacrylate-co-2-sulfoethyl methacrylate), 48:48:8 by weight, in 20 ml. of Solvesso 100. A liquid developer is made by combining 3.2 g. of Concentrate 16 with 3.4 ml. of Solution 16, and adding the mixture dropwise to 326 ml. of Isopar G. by the technique of the previous examples. When used to develop an electrostatic charge pattern by the method of the previous examples, the developer produces a high density image which transfers uniformly and completely to a transfer sheet. After extended use, when developed density falls off, the developer is readily replenished to its initial condition by adding an amount of Concentrate 16 and Solution 16 corresponding to the amount of pigment and resin which has deposited on the image-bearing members which have been developed.

Example 17

Concentrate 17 is prepared by milling as in the previous examples a 1 g. portion of the lithium salt of poly(ethyl acrylate-co-ethyl methacrylate-co-lauryl methacrylate-co-2-sulfoethyl methacrylate), 46:26:16:12 by weight, 1 g. of the pigment of Example 7, and 20 ml. of Solvesso 100. Solution 17 is the same as Solution 16 of the previous example. A liquid developer is made by combining 3.2 g. of Concentrate 17 with 5.1 ml. of Solution 16, and adding the resultant mixture to 324 ml. of Isopar G, dropwise. The developer has good density control, and forms a dense image on an electrostatic charge pattern carried on an electrophotographic imaging member. Transfer of the toner image to a paper transfer sheet gives virtually complete and uniform transfer.

Examples 18, 19, 20 and 21

Concentrates 18-21 are prepared from the lithium, barium, zinc and cobalt salts, respectively, of poly(ethyl acrylate-co-ethyl methacrylate-co-lauryl methacrylate-co-acrylic acid), 46:34:16:4 by weight. Each contains 1 g. of the polymer dissolved in 20 ml. of Solvesso 100, and also 1 g. of the pigment of Example 8. The salts are prepared by dissolving the polymer in water, adding a molar excess of the acetate of the appropriate metal, and isolating the polymer. Solutions 18-21 each contain 1 g. of the lithium salt of poly(styrene-co-lauryl methacrylate-co-methacrylic acid) dissolved in 20 ml. of Solvesso 100. Liquid developers are made by combining 3.2 g. of the appropriate concentrate with 5.1 ml. of one of the solutions, after milling the ingredients of the concentrates to form the concentrate, and dispersing the mixture under high shear into 323 ml. of Isopar G. The resulting developer is used to develop an electrostatic charge pattern on an organic photoconductive element, and the resultant image transfers well to a receiving element. Each of the developers has excellent replenishment characteristics.

Example 22

Concentrate 22 is prepared by milling as in previous examples a 1 g. portion of poly(butyl methacrylate-co-lauryl methacrylate-co-2-sulfoethyl methacrylate), 76:16:8 by weight, 1 g. of the pigment of Example 7, and 20 ml. of Solvesso 100. Solution 22 is prepared by dissolving 1 g. of poly(lauryl methacrylate-co-2-sulfoethyl methacrylate), 92:8 by weight, in 20 ml. of Solvesso 100. A liquid developer is made by mixing 3.2 g. of Concentrate 22 with 5.1 ml. of Solution 22 and adding the mixture thus prepared to 324 ml. of Isopar G under conditions of high shear. When used to develop electrostatic charge patterns, the developer gives high density and good marking characteristics. The image transfers cleanly and completely to a transfer sheet. Replenishment of the developer with addition of a suitable amount of Concentrate 22 and Solution 22 after some depletion has occurred restores the initial condition of the developer.

Type A polymers of the type hereinbefore described are also useful for stabilizing polymers known in liquid developers of the prior art. Such polymers may be of types chemically well characterized, or they may be trade-named polymers which may, in certain situations, have variable compositions. It has been found that in those situations in which the stability is marginal or poor, the Type A polymers herein described greatly enhance the stability and their use results in developers having exceptionally long life and good marking and transfer properties.

Example 23

Concentrate 23 is prepared in two separate parts by milling together, for each part, 16 g. of pigment, 14.4 g. of Beckosol 7, 53.2 g. Amberol ST-137 and 86.4 g. of Solvesso 100. The first part contains Rhodamine Y as pigment; the second, Cerise T (see Example 4 for a characterization of the pigments). Beckosol 7 is a soya modi-

fied alkyl sold by Reichold Chemicals, Inc. Amberol ST-137 is a reactive unmodified phenol formaldehyde resin sold by Rohm and Haas Company. The two parts are combined into a single concentrate. Solution 23 is prepared by dissolving 1 g. of the partial sodium salt of poly(styrene-co-lauryl methacrylate-co-3-sulfopropyl methacrylate), 46:50:4 by weight, in 100 g. of Solvesso 100. A 3.3 ml. portion of Concentrate 23 is mixed with a 25 ml. portion of Solution 23, and a liquid developer made therefrom by slowly adding the mixture to 472 ml. of Isopar G under high shear. An electrostatic charge pattern formed by exposing a charged organic photoconductive element to a continuous-tone image is then developed with the developer. A good reproduction of the image results. A developer prepared as above but without the terpolymer agglomerates immediately upon dispersion into the Isopar. When poly(styrene-co-lauryl methacrylate-co-dimethylaminoethyl methacrylate-co-2-sulfoethyl methacrylate), 44:43:6:7 by weight, is used in preparing Solution 23, a stable developer with negatively charged particles results. Carbon black may be used in place of colored pigments.

Example 24

Concentrate 24 is prepared by milling together 1 g. of poly(butyl methacrylate-co-lauryl methacrylate), 70:30 by weight, 1 g. of yellow pigment (C.I. 21100) and 20 ml. of Solvesso 100. Solution 24 is prepared by dissolving 1 g. of the sodium salt of poly(styrene-co-lauryl methacrylate-co-3-sulfopropyl methacrylate), 47:43:10 by weight, in 20 ml. of Solvesso 100. Concentrate 24 and 5.1 ml. of Solution 24 are mixed together and the mixture added gradually to 324 ml. of Isopar G under high shear, as before. There results a stable developer dispersion having good density control and capable of producing a dense image on an organic photoconductive element bearing an electrostatic charge pattern. If a developer is prepared not using Solution 24, the resultant mixture agglomerates immediately upon addition of the Concentrate to the Isopar.

Example 25

Three concentrates are prepared by milling together, for each concentrate, 1 g. of the pigment of Example 7 with 1 g. of polymer as follows and 20 ml. of Solvesso 100:

Concentrate	Polymer
25A ----	Poly(butylmethacrylate-co-lauryl methacrylate-co-acrylic acid), 80:16:4 by weight.
25B ----	Same; 76:16:8 by weight.
25C ----	Same; 72:16:2 by weight.

Three solutions are prepared, each containing 1 g. of the partial sodium salt of poly(styrene-co-lauryl methacrylate-co-3-sulfopropyl methacrylate), 50:46:4. One of the solutions is combined with one of Concentrates 25A, 25B and 25C, and each of the remaining two with one of the remaining concentrates. A 3.2 g. portion of concentrate and a 1.7 ml. portion of solution is used in each instance. The resulting mixture is slowly added to 328 ml. of Isopar G under high shear conditions as before to produce, for each concentrate, a separate liquid developer. Each of the developers thus obtained is used to develop an electrostatic charge pattern. A good reproduction of the pattern results in each case. Each image transfers cleanly and uniformly to a transfer sheet. Developers made using the concentrates alone in the absence of the resins contained in the solutions agglomerate immediately upon addition of the concentrate to the Isopar.

Example 26

Solution 26A is prepared by dissolving 1 g. of the lithium salt of poly(butyl methacrylate-co-2-sulfoethyl methacrylate) 88:12 by weight in 19.2 ml. of Solvesso 100. Solution 26B is prepared by dissolving 1 g. of the lithium salts of poly(styrene-co-lauryl methacrylate-co-

methacrylic acid) 50:46:4 by weight in 19.2 ml. Solvesso 100. A developer is prepared by combining 3.2 g. each of solutions 26A and 26B and diluting the combination with 326 ml. of Isopar G while stirring with a magnetic stirrer.

When flowed over the surface of an organic photoconductor element bearing an electrostatic charge pattern of negative polarity, the developer produces a virtually colorless image which can be inked and used as a lithographic printing plate or the image can be transferred to a hydrophilic surface and then inked.

Example 27.—Preparation of poly(styrene-co-lauryl methacrylate-co-lithium methacrylate)

In 80 ml. of dimethylformamide is dissolved 4 g. of lithium methacrylate followed by 50 g. of styrene, 46 g. of lauryl methacrylate and 1 g. of azobisisobutyronitrile. The solution is flushed with nitrogen and heated at 70° C. for 20 hours. The resultant polymer solution is diluted with 100 ml. of dioxane and poured into cold water with vigorous agitation to precipitate the product which has an inherent viscosity in chloroform of 0.3.

Example 28.—Preparation of poly(ethyl acrylate-co-ethyl methacrylate-co-lauryl methacrylate-co-sulfoethyl methacrylate, lithium salt)

Into 12 g. of sulfoethyl methacrylate in 200 ml. of dimethylformamide is stirred 2.6 g. of lithium hydroxide monohydrate until solution occurs. To the solution is added 46 g. of ethyl acrylate, 26 g. ethyl methacrylate, 16 g. of lauryl methacrylate and 2 g. of azobisisobutyronitrile. The solution is flushed with nitrogen and heated at 70° C. for 20 hours to form the polymer. Evaporation of the solvent gives a product which has an inherent viscosity in chloroform of 0.2.

Liquid developers can be prepared using the polymer and polymer mixtures described above without adding any colorant material such as pigment. In such case, solvent milling to blend together the pigment and the polymer is unnecessary. This type of liquid developer free from colorant may be used to develop permanent images from electrostatic charge patterns, which permanent images have little or no color. If one is interested simply in producing an ink-receptive image or forming a substantially colorless, patterned overcoat, this type of colorant-free liquid developer is quite useful.

The invention has been described in detail with particular reference to preferred embodiments thereof, but it will be understood that variations and modifications can be effected within the spirit and scope of the invention.

We claim:

1. A liquid developer for developing electrostatic charge patterns comprising (1) an electrically insulating organic carrier liquid, having a dielectric constant less than about 3.0 and a volume resistivity greater than about 10^{10} ohm-cm., in which styrene and alkyl acrylates having from about 1 to about 4 carbon atoms in the alkyl moiety are insoluble and (2) at least one polymer uniformly distributed throughout said carrier liquid, said polymer containing at least two monomeric moieties, at least one of said monomeric moieties being a polar moiety present in an amount of at least about 1.5×10^{-4} moles/g. of said polymer and at least one other of said monomeric moieties being a moiety soluble in said carrier liquid, said polymer containing a sufficient amount of the soluble moiety to yield a dispersibility ratio for said polymer in the liquid carrier greater than about 0.825, the polar moiety being selected from the group consisting of:

- sulfoalkyl acrylates;
- sulfoalkyl methacrylates;
- metal salts of sulfoalkyl acrylates;
- metal salts of sulfoalkyl methacrylates;
- amine salts of sulfoalkyl acrylates;
- amine salts of sulfoalkyl methacrylates;

(g) amine salts of acids selected from the group consisting of acrylic and methacrylic acids; and mixtures thereof.

2. A liquid developer for developing electrostatic charge patterns comprising (1) from about 85 to about 99 weight percent of an electrically insulating hydrocarbon carrier liquid, having a dielectric constant less than about 3 and a volume resistivity greater than about 10^{10} ohm-cm., in which styrene and alkyl acrylates having from about 1 to about 4 carbon atoms in the alkyl moiety are insoluble (2) a pigment or dyestuff colorant and (3) from about 0.1 to about 15 weight percent of at least one polymer uniformly distributed throughout said carrier liquid, said polymer containing at least two monomeric moieties, at least one of said monomeric moieties being a polar moiety present in an amount of at least about 1.5×10^{-4} moles/g. of said polymer and at least one other of said monomeric moieties being a moiety soluble in said carrier liquid, said polymer containing at least about 35 weight percent of the soluble moiety and less than about 20 percent by weight of the polar moiety, the polar moiety selected from the group consisting of:

- (a) sulfoalkyl acrylates;
- (b) sulfoalkyl methacrylates;
- (c) metal salts of sulfoalkyl acrylates;
- (d) metal salts of sulfoalkyl methacrylates;
- (e) amine salts of sulfoalkyl acrylates;
- (f) amine salts of sulfoalkyl methacrylates;
- (g) amine salts of acids selected from the group consisting of acrylic and methacrylic acids; and mixtures thereof.

3. The liquid developer described in claim 2 wherein the soluble moiety is selected from the group consisting of:

- (a) alkyl styrenes having from about 3 to about 10 carbon atoms in the alkyl moiety;
- (b) alkoxy styrenes having from about 3 to about 10 carbon atoms in the alkyl moiety;
- (c) alkyl acrylates having from about 8 to about 22 carbon atoms in the alkyl moiety;
- (d) alkyl methacrylates having from about 8 to about 22 carbon atoms in the alkyl moiety;
- (e) vinyl alkyl ethers having from about 8 to about 22 carbon atoms in the alkyl moiety; and
- (f) vinyl esters of aliphatic acids having from about 6 to about 22 carbon atoms in the alkyl moiety; and mixtures thereof.

4. The liquid developer described in claim 2 wherein the polar moiety is selected from the group consisting of:

- (a) sulfoalkyl acrylates having from 1 to about 4 carbon atoms in the alkyl moiety thereof;
- (b) sulfoalkyl methacrylates having from 1 to about 4 carbon atoms in the alkyl moiety thereof;
- (c) metal salts of sulfoalkyl acrylates having from 1 to about 4 carbon atoms in the alkyl moiety thereof, the metals forming said salts being selected from the group consisting of metals in Groups I, IIa, IIb and VIII of the Periodic Chart;
- (d) metal salts of sulfoalkyl methacrylates having from 1 to about 4 carbon atoms in the alkyl moiety thereof, the metals forming said salts being selected from the group consisting of metals in Groups I, IIa, IIb and VIII of the Periodic Chart;
- (e) amine salts of sulfoalkyl acrylates having from 1 to about 4 carbon atoms in the alkyl moiety thereof;
- (f) amine salts of sulfoalkyl methacrylates having from 1 to about 4 carbon atoms in the alkyl moiety thereof;
- (g) amine salts of acids selected from the group consisting of acrylic and methacrylic acids; and mixtures thereof.

5. A liquid developer according to claim 2 wherein said metal salts contain a metal selected from the group

consisting of sodium, lithium, potassium, copper, barium, zinc, cobalt, iron and magnesium.

6. The liquid developer described in claim 2 wherein said soluble moiety is selected from the group consisting of:

- (a) alkyl styrenes having from about 5 to about 10 carbon atoms in the alkyl moiety thereof;
- (b) alkyl acrylates having from about 12 to about 22 carbon atoms in the alkyl moiety thereof;
- (c) alkyl methacrylates having from about 12 to about 22 carbon atoms in the alkyl moiety thereof;
- (d) vinyl esters of aliphatic acids having from about 10 to about 22 carbon atoms in the alkyl moiety thereof; and mixtures thereof.

7. A liquid developer according to claim 2 wherein the polymer contains at least one substantially insoluble moiety.

8. The liquid developer described in claim 2 wherein the polymer contains at least one substantially insoluble moiety, said insoluble moiety is selected from the group consisting of:

- (a) a styrene selected from the group consisting of styrene, methyl styrene, methoxy styrene and a halogenated styrene;
- (b) alkyl acrylates having from about 1 to about 4 carbon atoms in the alkyl moiety;
- (c) alkyl methacrylates having from 1 to about 4 carbon atoms in the alkyl moiety;
- (d) vinyl alkyl ethers having from 1 to about 4 carbon atoms in the alkyl moiety;
- (e) vinyl esters of aliphatic acids having from about 1 to about 4 carbon atoms in the alkyl moiety; and mixtures thereof.

9. The liquid developer described in claim 2 wherein the polymer contains at least one substantially insoluble moiety, said insoluble moiety selected from the group consisting of:

- (a) styrene;
- (b) α -methyl styrene;
- (c) alkyl acrylates having from 1 to about 4 carbon atoms in the alkyl moiety thereof;
- (d) alkyl methacrylates having from 1 to about 4 carbon atoms in the alkyl moiety thereof;
- (e) vinyl esters of aliphatic acids having from 1 to about 4 carbon atoms in the alkyl moiety thereof; and mixtures thereof.

10. A liquid developer according to claim 9 wherein the polymer contains from about 35 to about 70 weight percent of said soluble moiety, from about 30 to about 65 weight percent of said insoluble moiety and from about 1.5 to about 16 weight percent of said polar moiety.

11. A liquid developer for developing electrostatic charge patterns comprising a carrier liquid consisting of an electrically insulating organic liquid, having a dielectric constant less than about 3 and a volume resistivity greater than about 10^{10} ohm-cm., in which styrene and alkyl acrylates having from about 1 to about 4 carbon atoms in the alkyl moiety are insoluble, said carrier liquid containing a pigment or dyestuff colorant and at least one polymer uniformly distributed throughout said carrier liquid, said polymer containing at least two monomeric moieties, at least one of said monomeric moieties being a polar moiety present in an amount of at least 1.5×10^{-4} moles/g. of said polymer and at least one other of said monomeric moieties being a moiety soluble in said carrier liquid, said polymer containing a sufficient amount of the soluble moiety to yield a dispersibility ratio for said polymer in the liquid carrier greater than about 0.825, the polar moiety being selected from the group consisting of:

- (a) sulfoalkyl acrylates;
- (b) sulfoalkyl methacrylates;
- (c) metal salts of sulfoalkyl acrylates;
- (d) metal salts of sulfoalkyl methacrylates;

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- (e) amine salts of sulfoalkyl acrylates;
- (f) amine salts of sulfoalkyl methacrylates;
- (g) metal salts of acids selected from the group consisting of acrylic and methacrylic acids;
- (h) amine salts of acids selected from the group consisting of acrylic and methacrylic acids; and mixtures thereof.

12. A liquid developer according to claim 11 wherein said soluble moiety is selected from the group consisting of:

- (a) alkyl styrenes having from about 3 to about 10 carbon atoms in the alkyl moiety;
- (b) alkoxy styrenes having from about 3 to about 10 carbon atoms in the alkyl moiety;
- (c) alkyl acrylates having from about 8 to about 22 carbon atoms in the alkyl moiety;
- (d) alkyl methacrylates having from about 8 to about 22 carbon atoms in the alkyl moiety;
- (e) vinyl alkyl ethers having from about 8 to about 22 carbon atoms in the alkyl moiety; and
- (f) vinyl esters of aliphatic acids having from about 6 to about 22 carbon atoms in the alkyl moiety; and mixtures thereof.

13. A liquid developer according to claim 11 comprising a third monomeric moiety which is substantially insoluble in said carrier liquid and selected from the group consisting of:

- (a) a styrene selected from the group consisting of styrene, methyl styrene, methoxy styrene and a halogenated styrene;
- (b) alkyl acrylates having from 1 to about 4 carbon atoms in the alkyl moiety;
- (c) alkyl methacrylates having from 1 to about 4 carbon atoms in the alkyl moiety;
- (d) vinyl alkyl ethers having from 1 to about 4 carbon atoms in the alkyl moiety; and
- (e) vinyl esters of aliphatic acids having from about 1 to about 4 carbon atoms in the alkyl moiety; and mixtures thereof.

14. A liquid developer for developing electrostatic charge patterns comprising a carrier liquid consisting of an electrically insulating organic liquid, having a dielectric constant less than about 3 and a volume resistivity greater than about 10^{10} ohm-cm., in which styrene and alkyl acrylates having from about 1 to about 4 carbon atoms in an alkyl moiety are insoluble, said carrier liquid containing a pigment or dyestuff colorant and at least one polymer uniformly distributed throughout said carrier liquid, said polymer containing at least 3 monomeric moieties, at least one of said monomeric moieties being a polar moiety present in an amount of at least 1.5×10^{-4} moles/gram of said polymer, at least one other of said monomeric moieties being a moiety insoluble in said carrier liquid, said polymer containing a sufficient amount of the soluble moiety to yield a dispersibility ratio for said polymer in the liquid carrier greater than about 0.825, the polar moiety being selected from the group consisting of:

- (a) sulfoalkyl acrylates having from 1 to about 4 carbon atoms in the alkyl moiety thereof;
- (b) sulfoalkyl methacrylates having from 1 to about 4 carbon atoms in the alkyl moiety thereof;
- (c) metal salts of sulfoalkyl acrylates having from 1 to about 4 carbon atoms in the alkyl moiety thereof, the metals forming said salts being selected from the group consisting of metals in Groups I, IIa, IIb and VIII of the Periodic Chart;
- (d) metal salts of sulfoalkyl methacrylates having from 1 to about 4 carbon atoms in the alkyl moiety thereof, the metals forming said salts being selected from the group consisting of metals in Groups I, IIa, IIb and VIII of the Periodic Chart;
- (e) amine salts of sulfoalkyl acrylates having from 1 to about 4 carbon atoms in the alkyl moiety thereof;

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- (f) amine salts of sulfoalkyl methacrylates having from 1 to about 4 carbon atoms in the alkyl moiety thereof;
- (g) amine salts of acids selected from the group consisting of acrylic and methacrylic acids; and mixtures thereof; and

said soluble moiety selected from the group consisting of:

- (a) alkyl styrenes having from about 5 to about 10 carbon atoms in the alkyl moiety thereof;
- (b) alkyl acrylates having from about 12 to about 22 carbon atoms in the alkyl moiety thereof;
- (c) alkyl methacrylates having from about 12 to about 22 carbon atoms in the alkyl moiety thereof;
- (d) vinyl esters of aliphatic acids having from about 10 to about 22 carbon atoms in the alkyl moiety thereof; and mixtures thereof; and

said insoluble moiety selected from the group consisting of:

- (a) styrene;
- (b) α -methyl styrene;
- (c) alkyl acrylates having from 1 to about 4 carbon atoms in the alkyl moiety thereof;
- (d) alkyl methacrylates having from 1 to about 4 carbon atoms in the alkyl moiety thereof;
- (e) vinyl esters of aliphatic acids having from 1 to about 4 carbon atoms in the alkyl moiety thereof; and mixtures thereof.

15. A liquid developer according to claim 2 comprising a second polymer, said second polymer containing at least two monomeric moieties, at least one of said monomeric moieties of said second polymer being a polar moiety and at least one other of said monomeric moieties of said second polymer being substantially insoluble in said carrier liquid, said substantially insoluble moiety comprising at least about 55 percent by weight of said second polymer, said polar moiety comprising between 0.5 and 20 percent by weight of said second polymer, the polar moiety being selected from the group consisting of:

- (a) sulfoalkyl acrylates;
- (b) sulfoalkyl methacrylates;
- (c) metal salts of sulfoalkyl acrylates;
- (d) metal salts of sulfoalkyl methacrylates;
- (e) amine salts of sulfoalkyl acrylates;
- (f) amine salts of sulfoalkyl methacrylates;
- (g) acids selected from the group consisting of acrylic and methacrylic acids;
- (h) metal salts of acids selected from the group consisting of acrylic and methacrylic acids;
- (i) amine salts of acids selected from the group consisting of acrylic and methacrylic acids;
- (j) aminoalkyl methacrylates and acrylates; and mixtures thereof.

16. A liquid developer for developing electrostatic charge patterns comprising a carrier liquid consisting of an electrically insulating hydrocarbon liquid, having a dielectric constant less than about 3 and a volume resistivity greater than about 10^{10} ohm-cm., in which styrene and alkyl acrylates having from about 1 to about 4 carbon atoms in the alkyl moiety are insoluble, said carrier liquid containing at least a first and second polymer uniformly distributed throughout said carrier liquid, said first polymer containing at least three monomeric moieties comprising a polar moiety, a soluble moiety, and a substantially insoluble moiety as follows:

- (a) at least about 1.5×10^{-4} moles/g. of said first polymer being a polar moiety selected from the group consisting of:
 - (1) sulfoalkyl acrylates having from 1 to about 4 carbon atoms in the alkyl moiety thereof;
 - (2) sulfoalkyl methacrylates having from 1 to about 4 carbon atoms in the alkyl moiety thereof;

- (3) metal salts of sulfoalkyl acrylates having from 1 to about 4 carbon atoms in the alkyl moiety thereof, the metals forming said salts being selected from the group consisting of metals in Groups I, IIa, IIb and VIII of the Periodic Chart; 5
- (4) metal salts of sulfoalkyl methacrylates having from 1 to about 4 carbon atoms in the alkyl moiety thereof, the metals forming said salts being selected from the group consisting of metals in Groups I, IIa, IIb and VIII of the Periodic Chart; 10
- (5) amine salts of sulfoalkyl acrylates having from 1 to about 4 carbon atoms in the alkyl moiety thereof; 15
- (6) amine salts of sulfoalkyl methacrylates having from 1 to 4 carbon atoms in the alkyl moiety thereof; 15
- (7) amine salts of acids selected from the group consisting of acrylic and methacrylic acids; and mixtures thereof; 20
- (b) a sufficient amount of the soluble moiety to yield a dispersibility ratio for said first polymer in the liquid carrier greater than about 0.825, the soluble moiety selected from the group consisting of: 25
- (1) alkyl styrenes having from about 5 to about 10 carbon atoms in the alkyl moiety thereof;
 - (2) alkyl acrylates having from about 12 to about 22 carbon atoms in the alkyl moiety thereof;
 - (3) alkyl methacrylates having from about 12 to about 22 carbon atoms in the alkyl moiety thereof; and 30
 - (4) vinyl esters of aliphatic acids having from about 10 to about 22 carbon atoms in the alkyl moiety thereof; and mixtures thereof; and 35
- (c) the substantially insoluble moiety selected from the group consisting of: 40
- (1) styrene;
 - (2) α -methyl styrene;
 - (3) alkyl acrylates having from 1 to about 4 carbon atoms in the alkyl moiety thereof; 40
 - (4) alkyl methacrylates having from 1 to about 4 carbon atoms in the alkyl moiety thereof; and 45
 - (5) vinyl esters of aliphatic acids having from 1 to about 4 carbon atoms in the alkyl moiety thereof; and mixtures thereof; 45
- and said second polymer containing at least three monomeric moieties comprising a polar moiety, a soluble moiety, and a substantially insoluble moiety as follows:
- (a) from about 0.5 to about 20 weight percent of a polar moiety selected from the group consisting of: 50
- (1) sulfoalkyl acrylates having from 1 to about 4 carbon atoms in the alkyl moiety;
 - (2) sulfoalkyl methacrylates having from 1 to about 4 carbon atoms in the alkyl moiety; 55
 - (3) metal salts of sulfoalkyl acrylates having from 1 to about 4 carbon atoms in the alkyl moiety thereof, the metals forming said salts being selected from the group consisting of metals in groups I, IIa, IIb, and VII of the Periodic Chart; 60
 - (4) metal salts of sulfoalkyl methacrylates having from 1 to about 4 carbon atoms in the alkyl moiety thereof, the metals forming said salts being selected from the group consisting of metals in Groups I, IIa, IIb, and VIII of the Periodic Chart; 65
 - (5) amine salts of sulfoalkyl acrylates having from 1 to about 4 carbon atoms in the alkyl moiety thereof;
 - (6) amine salts of sulfoalkyl methacrylates having from 1 to about 4 carbon atoms in the alkyl moiety thereof; 70
 - (7) acids selected from the group consisting of acrylic and methacrylic acids;
 - (8) metal salts of acids selected from the group 75

- consisting of acrylic and methacrylic acids, the metals forming said metal salts being selected from the group consisting of metals in Groups I, IIa, IIb and VIII of the Periodic Chart;
- (9) amine salts of acids selected from the group consisting of acrylic and methacrylic acids;
- (10) aminoalkyl acrylates having from 1 to about 4 carbon atoms in the alkyl moiety thereof, the amino group being an alkylamino in the alkyl moiety thereof, and
- (11) aminoalkyl methacrylates having from 1 to about 4 carbon atoms in the alkyl moiety thereof, the amino group being an alkylamino having from 1 to about 4 carbon atoms in the alkyl moiety thereof; and mixtures thereof; and
- (b) from about 10 to about 25 weight percent of a moiety soluble in said carrier liquid and selected from the group consisting of:
- (1) alkyl styrenes having from about 5 to about 10 carbon atoms in the alkyl moiety thereof;
 - (2) alkyl acrylates having from about 12 to about 22 carbon atoms in the alkyl moiety thereof;
 - (3) alkyl methacrylates having from about 12 to about 22 carbon atoms in the alkyl moiety thereof; and
 - (4) vinyl esters of aliphatic acids having from about 10 to about 22 carbon atoms in the alkyl moiety thereof; and mixtures thereof; and
- (c) from about 60 to about 85 weight percent of a moiety substantially insoluble in said carrier liquid and selected from the group consisting of:
- (1) styrene;
 - (2) α -methyl styrene;
 - (3) alkyl acrylates having from 1 to about 4 carbon atoms in the alkyl moiety thereof;
 - (4) alkyl methacrylates having from 1 to about 4 carbon atoms in the alkyl moiety thereof; and
 - (5) vinyl esters of aliphatic acids having from 1 to about 4 carbon atoms in the alkyl moiety thereof; and mixtures thereof.
17. The liquid developer described in claim 16 wherein said developer contains a colorant.
18. The liquid developer described in claim 16 wherein the polar moiety in said first polymer is a moiety selected from the group consisting of sulfoalkyl methacrylates, metal salts of sulfoalkyl methacrylates, sulfoalkyl acrylates, and metal salts of sulfoalkyl acrylates the polar moiety in said second polymer is a moiety selected from the group consisting of sulfoalkyl methacrylates, metal salts of sulfoalkyl methacrylates, acrylic acid, metal salts of methacrylic acid and amino alkyl methacrylates, said soluble moiety in each of said first and said second polymers is a moiety selected from the group consisting of alkyl methacrylates having from about 12 to about 18 carbon atoms in the alkyl moiety and alkyl acrylates having from about 12 to about 18 carbon atoms in the alkyl moiety, and said substantially insoluble moiety in each of said first and second polymers is a moiety selected from the group consisting of styrene, an alkyl acrylate having from 1 to about 4 carbon atoms in the alkyl moiety and an alkyl methacrylate having from 1 to about 4 carbon atoms in the alkyl moiety.
19. The liquid developer described in claim 16 wherein said first polymer contains at least a polar moiety selected from the group consisting of sulfoethyl methacrylate and its partial sodium salt, sulfopropyl methacrylate and its partial sodium salt, and the lithium salt of sulfoethyl methacrylate, a soluble moiety selected from the group consisting of lauryl methacrylate and octadecyl methacrylate and a substantially insoluble moiety selected from styrene, and said second polymer contains at least a polar moiety selected from the group consisting of sulfoethyl methacrylate, the lithium salt of sulfoethyl methacrylate, dimethylaminoethyl methacrylate, acrylic acid, and the barium, lithium, zinc and cobalt salts of methacrylic acid,

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a soluble moiety selected from the group consisting of lauryl methacrylate and octadecyl methacrylate, and a substantially insoluble moiety selected from the group consisting of ethyl acrylate, ethyl methacrylate and butyl methacrylate.

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U.S. Cl. X.R.

260—47, 80.8, 86.1, 80.3, 85.7, 79.5

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,788,995 Dated January 29, 1974

Inventor(s) Frederick A. Stahly and Steward H. Merrill

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

Column 5, line 73, "Zince" should read --Zinc--;

Column 6, line 64, "Alkll" should read --Alkyl--;

Column 7, line 27, "prsent" should read --present--;

Column 8, line 56, "electristatic" should read --electrostatic--;

Column 14, line 53, the word --high-- should be inserted after the word having;

Column 17, line 18, the part of the sentence reading "dissolving g." should read --dissolving 1 g.--;

Column 17, line 33, after the word developer, insert --.---;

Column 17, line 47, "5" should read --15--;

Column 17, lines 57 and 58, after the words methacrylate-co-, insert --lauryl methacrylate-dimethylaminoethyl methacrylate-co- --;

Column 17, line 65, the period "." should be deleted after the word, Isopar G;

Column 23, line 59, "sulfoalkl" should read --sulfoalkyl--;

Column 25, line 60, "VII" should read --VIII--.

Signed and sealed this 17th day of September 1974.

(SEAL)
Attest:

McCOY M. GIBSON JR.
Attesting Officer

C. MARSHALL DANN
Commissioner of Patents