

[54]	LIQUID TONERS WITH AN AMPHIPATHIC GRAFT TYPE POLYMERIC MOLECULE	3,639,243	2/1972	Okuno	252/62.1
		3,639,244	2/1972	Machida	252/62.1
		3,669,886	6/1972	Kosel	252/62.1

[75] Inventor: **George E. Kosel**, Park Ridge, N.J.

[73] Assignee: **Philip A. Hunt Chemical Corporation**, Palisades Park, N.J.

[22] Filed: **Apr. 30, 1973**

[21] Appl. No.: **355,567**

Related U.S. Application Data

[60] Division of Ser. No. 7,253, Jan. 30, 1970, abandoned, which is a continuation-in-part of Ser. No. 810,841, March 26, 1969, abandoned.

[52] U.S. Cl. **252/62.1; 96/1 LY; 117/37 LE**

[51] Int. Cl. **G03g 9/04**

[58] Field of Search **96/1 LY; 117/37 LE; 260/22, 33.6; 252/62.1**

References Cited

UNITED STATES PATENTS

3,391,014 7/1968 Fauser 252/62.1

Primary Examiner—Norman G. Torchin

Assistant Examiner—John L. Goodrow

Attorney, Agent, or Firm—Kirschstein, Kirschstein, Ottinger & Frank

[57]

ABSTRACT

A liquid toner with a number of solids less than those conventionally used in a multi-component liquid toner, obtained by combining the functional characteristics of plural previous different kinds of solids into a complex molecule, thereby obtaining better image fixation, improved resistance to preferential depletion, improved image definition, clear background, improved shelf life, improved functional life and a broad color range.

26 Claims, No Drawings

LIQUID TONERS WITH AN AMPHIPATHIC GRAFT TYPE POLYMERIC MOLECULE

CROSS-REFERENCE TO RELATED APPLICATION

This is a division of application Ser. No. 7,253 filed Jan. 30, 1970 now abandoned which is a continuation-in-part of application Ser. No. 810,841 filed March 26, 1969 for LIQUID TONERS, now abandoned.

BACKGROUND OF THE INVENTION

1. Field of the Invention

A liquid toner including an amphiphatic molecule made up of various polymeric moieties having different functions, of which one may be to impart a color, that are desirable for toner use, at least one of which is solvated and another non-solvated by a liquid carrier system.

2. Description of the Prior Art

Prior art liquid toners as well as liquid toners of the present invention can be used for several purposes which can be generally grouped under the heading of selective deposition on a substrate. For example, the toners can be employed to form on a sheet a visible pattern which may be a picture, including a half-tone picture, a line picture, or a photographic reproduction or a symbol, or a digit, or a graph, or a letter of an alphabet. The widest present-day use of liquid toners and the principal use of the liquid toner of the present invention is as a liquid electrostatographic developer for office copy apparatus. However, it is to be understood that the liquid toners of the present invention are not thus limited in their utility and may also be employed for high speed print-outs and reproductions, ink jet printing, enlarged reproductions of microfilms, facsimile printing, instrument recording, etc.

Prior art liquid toners can, in general, be categorized into two classes which for convenience will be referred to as conventional liquid toners and liquid toners based on toner powders.

A conventional liquid toner constitutes a dispersion of pigments, the dispersed phase, in a liquid hydrocarbon system, the continuous phase. The liquid hydrocarbon system conventionally is characterized by the attributes of: (a) quick evaporation, that is to say, a thin film of this system will evaporate in a few seconds at a temperature below the char point of paper, so as to permit fast drying; (b) nontoxicity when applied to the human skin or inhaled along with air; (c) low odor, so that it can be used in a machine which is located in an ill-ventilated room; (d) full drying, i.e., when employed with film forming agents, it will fully escape from a deposited film, so as to leave the film liquid-free and not subject to evaporation over protracted periods of time after a deposited graphic representation is seemingly dry; (e) sufficient fluidity to allow the particles of solid suspended material which are to be attracted to a copy sheet for the formation of a graphic representation to migrate therethrough with ease, so that, particularly where such material is electrostatographically attracted, it can be quickly attracted to and coupled with the patterning of electrostatic charges which is to be visibly reproduced by development with the toner; (f) physical and chemical inertness to the coating binder used on copy sheets, so that it will not attack the same; (g) the ability not to bleed off the electrostatic charges on the copy sheet before the graphic representation is

visually formed, whereby to maintain any desired degree of contrast; and (h) low cost.

Typically, the liquid hydrocarbon system has been a petroleum fraction which inherently includes the aforesaid attributes. Such fraction preferably has had certain specific physical characteristics which are the same as those of a preferred liquid carrier system used in the present invention and which, since the same will be described in detail hereinafter, will not be listed at this point.

The continuous phase (liquid system) of a conventional liquid toner has had present therein, some dissolved in it and others suspended in it, certain solids which have functional attributes that are desirable for proper operation of the process involved, usually electrostatographic development. These solids are: (a) pigment particles; (b) a fixative which usually is a thermoplastic resin, the ability to flow under heat being sometimes desirable to increase the bond between the selectively deposited material and the copy sheet by subjecting the substrate with deposited material thereon to a temperature sufficiently high to fuse the deposited material and thereby improve its interphase relationship with the substrate; (c) a dispersant which usually is a long chain organic compound such as a synthetic polymer with some oil soluble and some polar groups, e.g., FOA 2, lube oil 564 and lecithin, these substances being specifically identified in copending application Ser. No. 767,031 filed Sept. 11, 1968 for LIQUID DEVELOPER FOR ELECTROSTATOGRAPHY, now U.S. Pat. No. 3,669,886 issued June 13, 1972, the purpose of the dispersant being to disperse solid particles present, e.g., the pigment particles, so as to prevent them from settling, this lengthens the shelf life, prevents caking and is believed to enhance the ability of the solid particles present to migrate through the continuous phase, and (d) a charge director which usually is a metallic derivative of a fatty acid or a resin acid. Typical pigment particles, fixatives, charge directors and dispersants are detailed in the aforesaid application Ser. No. 767,031. The charge director is adsorbed by the individual pigment particles and behaves in some manner, the physical explanation for which is not fully comprehended but is believed to be a surface phenomenon, to cause pigment aggregates to be formed in the dispersed phase. The dispersion of these aggregates is stabilized by the dispersant via an entropic repulsion mechanism. The foregoing is an extremely condensed description of conventional toners, very broadly considered and without detailing the many sophisticated approaches that have been made in attempts to obtain commercially acceptable conventional liquid toners.

The second type of liquid toner, to wit, the one based on toner powders utilizes a preground dry toner powder, such as a finely comminuted electroscopic colored material, for instance, a mixture of carbon black and polystyrene, as the dispersed phase, and a liquid hydrocarbon system, such as the one above described, as the continuous phase. The toner powders of the second type of liquid toner are distinguished from the pigments used in conventional liquid toners in that the order of particle size of the toner powders used in the second type of liquid toner is two to three orders larger than the particle size of the pigments in a conventional liquid toner. The continuous phase of liquid toners based on toner powders usually contains a charge director which commonly is dissolved or dispersed in the continuous phase and the continuous phase generally is of

a higher viscosity than is the continuous phase of a conventional toner, so as to hinder, i.e. impede, the settling of these large toner particles. The second type of liquid toner also usually contains a fixative.

Both of these conventional types of liquid toners have certain inherent defects which largely are caused by the fact that (a) the solid components of the toners constitute several compounds, some of which have overlapping functions, but each of which is highly desirable or even necessary for different major functions, and (b) unevenness of particle size of undissolved particles.

One defect is the particle size distribution of the dispersed phase. In conventional toners not all of the pigment particles of the dispersed phase are included in the aggregates formed under the influence of the charge director. For reasons as yet undetermined by physical chemists, some of these pigment particles are suspended relatively free of other particles and of aggregates. These unaggregated particles are of very small size, probably in the millimicron size range, and sometimes are referred to as "fines". They tend to be deposited in non-image areas and create an overall light colored, e.g., grayish, background that distinguishes liquid toners from dry toners. It is well recognized in the art that the background discoloration is far less noticeable with dry toners than with liquid toners and this is one of the principal reasons that liquid toners have had great difficulty in making a deep inroad in apparatuses employing toners.

With toner powder based liquid developers, with their larger particle size, the particle size distribution of the dispersed phase is more uniform so that the background areas are virtually free of toner particle deposition; however, because of the very largeness of the particle size, it has not been possible to develop formulations which prevent the toner particles from settling out so that the shelf life of these latter developers is relatively short and the deposited particles tend to cake, making it difficult after they have stored for any appreciable length of time to redisperse them easily and quickly by shaking. Not only that but this large particle size tends to lead to poor resolution, so that small details are lost or are obliterated, i.e., run together into larger areas of a graphic representation. It would be ideal, although this has not been accomplished before the present invention, to have a mono-dispersed particle size distribution, i.e., a substantially identical particle size of the dispersed phase which is larger than that present in a conventional toner, so as to eliminate fines, but smaller than that of the toner powder based liquid developers, so as to secure satisfactory resolution and inhibit settling unless the settling can be otherwise controlled.

Another defect of previous liquid toners arises from the fact that the liquid toner is used in an apparatus that is in continuous operation. As the apparatus functions on a minute to minute, hour to hour and day to day basis, the liquid toner is being used up and must be replenished. Superficially, this might seem to be a simple matter. It would appear that all one would have to do is add more of the solids and/or more of the continuous phase, either in the form of more liquid toner, more liquid system, or a concentrate of liquid toner. However, due to various causes, the sundry components of a liquid toner chemical system, and particularly of a liquid electrostatographic system, deplete at different rates, the rates fluctuating, for instance, as functions of the

stress applied to the liquid toner system, for example, more or less image area per print, and more or less solvent carry-out per print, this latter being dependent on developer tray configuration, roller tension, bath volume, overflow, recirculation rate and paper velocity. Other causes are the different volatilization rates of the different compounds, the temperature of the developing stage, the different rates of print pick up for the different compounds, and the different potentials of different parts of the latent electrostatic image. These causes are not intended to be a complete list of all of the variables which causes the components to be depleted at different rates.

Thus, as a practical matter, it is physically impossible to replenish such a liquid toner system in a manner such as to maintain it at its optimum capability even for the major part of its life. The more components that are present a system, and as will be realized from the aforesaid description of the prior art liquid toners there are many components, the worse this problem of preferential depletion and replenishment becomes. It simply is not practical to replenish the various components at the different rates at which they are depleted. To do this, even on one machine, would be an economic waste. To do it generally on copy machines is utterly impractical. Hence, as a tolerable practice, it has been customary to replenish liquid toners with concentrates having roughly the proportions of the solids in the original liquid toners, whereby as the replenished toner in the apparatus is used more and more, the quality of the patterned deposit progressively is degraded until finally a point is reached where whatever liquid toner is present in the equipment is discarded and a completely fresh bath of liquid toner substituted for the same. Prior to the present invention, it has not been possible to solve this problem because the number of solid components could not be minimized.

Another problem which has seriously plagued various types of electrostatic apparatuses that employ a liquid toner is slow fixing speed. This becomes most noticeable and serious in equipment which is required to deliver electrostatically developed material at extremely high rates of speed. At the present time it requires several minutes for an electrostatically developed image to be sufficiently dried, in the absence of a separate heater, to be handled in equipment, e.g., by rolling up or fanfolding, without smearing the freshly developed print. To avoid this, resort often has been had to extremely high output heaters which unnecessarily complicate and raise the prices of the equipment and call for considerable amounts of space as well as cooling mechanisms and high-power electric lines. All of this has retarded the widespread use of liquid toners. This initial smearability of electrostatically developed image is not to be confused with the smearability of fully dried images, e.g., copies in the hands of a user to whom substrates such as paper bearing these images are delivered possibly hours or days later.

Furthermore, the same problem of the inability of present liquid toners to be rapidly initially fixed is present in computer read-outs and like equipment which deliver information at very rapid rates. A computer is capable of delivering literally billions of characters per second. But there is no liquid toner which can begin to approximate development thereof at an equivalent speed. About the best that can be done with presentday equipment is 90 - 120 inches of copy per minute, or 9,000 sheets per hour, and often this requires other

types of printing, i.e., printing not using electrostatic methods, e.g., impact printing. It would be extremely desirable to provide an electrostatic liquid toner which is capable of very rapid fixation, i.e., fixation which renders an image virtually smear-proof to mechanical handling within 20 seconds after leaving a development bath.

A further problem in the prior art in connection with liquid electrostatic toners is the difficulty the art has had, despite conscientious attempts to provide the same, to supply a liquid toner which is capable of being efficiently issued as a jet and electrostatically directed. To date the only such toners available are subject to many drawbacks which, although indicating the tremendous commercial feasibility of this new style of printing, have not yet rendered it sufficiently acceptable for general commercial use.

SUMMARY OF THE INVENTION

It is an object of the present invention to provide an improved and unique liquid toner having a mono-dispersed phase of a particle size which is intermediate those of the fines of conventional toners and those of the pigment particles of toner based liquid toner powders, i.e., in excess of $25\text{m}\mu$ and not greater than 25μ and a reduced number of kinds of solid components present in this mono-dispersed phase, whereby to reduce and to minimize the preferential depletion of toners of the prior art types.

It is another object of the invention to provide a liquid toner of the character described which has a superior fixation of the selective deposition so that the same will be virtually smear-proof.

It is another object of the invention to provide a liquid toner of the character described which has a substantially improved resistance to preferential depletion of component parts of the liquid toner during its use, e.g., in a reproduction machine that is employed in either continuous or intermittent operation.

It is another object of the invention to provide a liquid toner of the character described having a selective deposition definition as good as that of a conventional toner and yet with virtual elimination of background color, that is to say, elimination of non-image area deposition of colored particles.

It is another object of the invention to provide a liquid toner of the character described which has an improved and, indeed, to all intents and purposes, an indefinite, resistance to settling so that there is a concomitant greatly increased shelf life.

It is another object of the invention to provide a liquid toner of the character described having an improved functional life, that is to say, a liquid toner which will provide more square inches of selective deposition than previous toners per unit of solids with a decreased frequency of replenishment and an improved economic and efficient utilization of the toner.

It is another object of the invention to provide a liquid toner of the character described which can be based upon any solvent system that is useful in a liquid toner employing apparatus, that is to say, any solvent system which is compatible with the apparatus being employed and the demands of the selective deposition method, as, for example, any solvent system that can be used to develop an electrostatographic image.

It is another object of the invention to provide a liquid toner of the character described which is capable of

making visible selective depositions of any desired color and any desired depth of color.

It is another object of the invention to provide a liquid toner of the character described which is particularly fast-setting in its initial stages so as to rapidly leave an image which, although still fresh, is smear-proof for machine handling, so that a substrate on which this image has been deposited can, within a comparatively short time, e.g., as little as 20 seconds, be safely manipulated without fear of spoiling the image, as, for instance, it can be rolled up or manifolded.

It is another object of the invention to provide a liquid toner of the character described which, by virtue of its very fast initial fixing, can be employed in electrostatic image development in equipment which has extremely high speed outputs of substrates bearing images, such, for instance, as computer read-outs or cathode ray tube read-outs or facsimile read-outs or read-outs of enlarged microfilms or read-outs of mirrordeflected light beams.

It is another object of the invention to provide a liquid toner of the character described which can be used with great facility in ink jet recording; that is to say, a liquid toner which in a droplet jet-beam form is capable of being facily manipulated by electrostatic deflecting arrangements.

It is another object of the invention to provide a liquid toner of the character described with which excellent results can be secured outside of the office copy field, in particular in connection with high speed electrostatic developing, although the toner is capable of efficiently handling all normal slower speed electrostatic developing.

It is another object of the invention to provide a liquid toner of the character described which functions in an excellent manner with all types of substrates and all types of latent electrostatic image recordings, e.g., which will function well with substrates including any kind of electrographic materials; examples of various types are conventional zinc oxide resin substrates, organic photoconductive substrates, titanium dioxide resin substrates and a substrate constituting a terephthalate dielectric sheet having a latent electrostatic image thereon imparted by a cathode ray pin tube. The substrates embraced within the scope of those which can be employed with the toner of the present invention may either be actinically sensitive or non-actinically sensitive, that is to say, the charged substrates can be sensitive to discharge by exposure to light or may not be thus sensitive.

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

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

DESCRIPTION OF THE PREFERRED EMBODIMENTS

In general, the several objects of the present invention are accomplished by providing a liquid toner which essentially consists of a solvent system, a color agent and a complex molecule including plural polymeric moieties of which at least one is solvated by the solvent system and at least one is non-solvated by the solvent system, the color agent optionally being in the form of a moiety of the molecule in the nature of a

chromophore. At least one of the moieties is of a resinous nature and serves as a fixative. A non-solvated moiety provides a solid particle in the solvent system (the continuous phase) enabling the desired size of particles to be formed and permitting electrophoretic deposition to take place in the formation of a patterned deposit on a substrate, e.g., enabling electrostatic attraction to take place between a particle and a latent electrostatic image on a copy sheet. The solvated moiety functions to maintain the complex molecule in suspension, that is to say, to prevent settling of the molecule and hence, in effect, operates as a dispersing agent. Thus, in the complex molecule, several functions of previously different solid compounds are amalgamated. It should be observed that the moiety or moieties which impart the resinous characteristic to the complex molecule may be either the solvent solvated moiety or the solvent non-solvated moiety or both. This complex molecule is a so-called "tailored" molecule, that is to say, it is an artificially created molecule which in a single compound provides plural functions heretofore requiring the presence of plural separate solids which resulted in preferential depletion and non-uniform or gross pigment particle size. A charge director is an additional most desirable component of the liquid toner.

The basic building block of the novel liquid toner of the present invention is the solvent system. The term "basic building block" is not used in the sense that the solvent system is the core of the complex molecule which is employed pursuant to the present invention, but rather that the nature of the solvent system influences the particular type complex molecule that is to be employed. Once the solvent system has been chosen, certain parameters of the liquid toner developer solid components, and specifically of the complex molecule, are indicated. Any type of solvent system can be used which is compatible with the particular apparatus and method using any specific form of a liquid toner embodying the present invention. For instance, the liquid toner of the present invention could be based upon a non-polar solvent system such as is conventionally employed in the creation of most patterned deposits and is widely used in electrostatographic toners. Nevertheless, the present invention is not limited to a non-polar solvent system and can be equally well used with a polar solvent system, where such a system is practical in any specific apparatus or method that can make use of such a toner. Because the present large-scale commercial use of liquid toners is with apparatuses and methods that utilize non-polar solvents, the following description of the invention as to the particular examples and compositions stresses solids used with a non-polar continuous phase, i.e., solvent system.

Such a non-polar solvent system includes an organic non-polar liquid having the characteristics of those previously mentioned above and referred to in particular under subdivisions (a) - (h) which are incorporated here by reference. An excellent and conventional solvent which is well known and widely used in liquid electrostatographic toners is a petroleum fraction, this having the attributes just mentioned. The petroleum fraction, i.e., the solvent system, in addition to having the aforesaid generalized physical attributes, has an evapo-

ration rate at least as fast as that of kerosene, but slower than that of hexane. Thereby, the evaporation of the liquid from a film will be rapid, e.g., two seconds, at a temperature slightly below the char point of paper, it being customary to raise the temperature of the film of liquid toner to this level for the purpose of evaporating the toner solvent after the patterned deposition has been formed by attraction to an electrostatically charged image. The petroleum fraction has a low K.B. (Kauri-butanol) number, to wit, less than 35, and preferably between 26 and 35. This low K.B. number minimizes the possibility that the petroleum fraction will attack the coating binder, e.g., the binder for the zinc oxides used in electrostatography, or will attack any sizing on the sheet, e.g., paper, upon which the coating is applied. The petroleum fraction also is substantially free of aromatic liquid constituents, e.g., is substantially aromatic-liquid-free. This term, as used herein, connotes that the proportion of aromatic liquids in the organic liquid carrier is not in excess of two per cent by weight. The aromatic liquids have a strong tendency to attack the coating binders, e.g., the coating binders for zinc oxide, but in concentrations of less than two per cent this tendency is so negligible as to be unnoticeable. The petroleum fraction has a high electrical resistivity, e.g., in the order of at least 10^9 ohm centimeters, and a dielectric constant of less than three and one-half, so that the liquid carrier will not dissipate the pattern of electrostatic charges which are to be developed in electrostatography. The TCC (Tagliabue closed cup) flash point of the liquid carrier is at least 100°F. and preferably about 120°F. to 152°F., whereby under the conditions of use the liquid is considered non-flammable. The paraffinic solvent also is nontoxic. It possesses no objectionable odor and preferably is odor-free, this being denoted by the term "low odor". Consonant with its low dielectric constant and high resistivity, the liquid carrier is non-polar. The liquid carrier has a low viscosity for the purpose of permitting rapid migration therethrough of non-dissolved particles and moieties which are to be attracted in large number to the electrostatically charged image which is to be developed. Such viscosity is between 0.5 and 2.5 centipoises at room temperature. The petroleum fraction also is inexpensive.

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

	Distillation	Dry End	Flash Pt.		Aniline Pt. °F.	Sp.Gr. 60°/60°F.
	IBP*		°F. TCC	K.B. No.		
	°F.	Pt. °F.				
Shell Sol 71	345	398	121	26.5	183	0.7563
Isopar H	350	371	123	26.9	183	0.7571
Isopar K	349	383	126	26.5	185	0.7587
Isopar L	372	406	144	—	187	0.7674
Amsco OMS	352	386	125	27.0	184.5	0.7608
Amsco 460 Solvent	375	456	150	34.5	146.5	0.8108
Amsco Odorless Insecticide Base	375	482	152	26.5	175.0	0.7711

*Initial Boiling Point ASTM D-1078

The nub of the invention consists in the use with the solvent system of a complex molecule having the polymeric moieties mentioned above. Hence, the liquid toner is basically a latex toner, which is to say, a toner that looks like a natural latex in that it constitutes a liquid continuous phase having the desired attributes for use in a patterned deposition system, together with a dispersed phase which is an amphipathic polymer. The term "latex" as used herein refers to a colloidal suspension of a synthetic polymer in any liquid, for instance, as prepared by emulsion or suspension polymerization. An "amphipathic" substance is one that has an affinity for two different materials, for instance, oil or water, or two different phases, so that one polymeric moiety of the amphipathic polymer, which is the foregoing complex molecule, will be solvated by the phase for which it has an affinity, which, in this instance, is the solvent system, and another polymeric moiety will not be solvated by this same phase, that is to say, will be insoluble in this phase, so that the phenomenon is created when the amphipathic polymer is contained in the solvent system of at least one moiety of the polymer being solvated by the solvent system and at least one moiety being non-solvated by the solvent system. The amphipathic polymer combines in one complex molecule the fixing agent, which is one or more of the moieties, the dispersing agent, which is one or more of the moieties, and optionally, a color agent, which is one or more of the moieties. This complex molecule, i.e., amphipathic polymer, by virtue of the fact that it is a molecule rather than a composition including a mixture of pigment particles, creates a narrow range of size distribution of the nonsolvated particles which ultimately are deposited on a substrate, e.g., a copy sheet, as by electrostatographic development, to create a patterned deposition. Desirably the particle size distribution of the non-solvated particles in the liquid toner of the invention is within two orders of magnitude and preferably is within about one order of magnitude. The foregoing ranges are what is denoted by the term "mono-dispersed".

The liquid toner, which is to say the latex system of the present invention, is created generally as follows. Firstly, the solvent system is chosen, for example, a non-polar solvent such as a petroleum fraction like the ones mentioned above, although as previously observed, other solvents could be used, e.g., polar solvents such as water.

It is appropriate to mention at this point that patterned depositions utilizing electrostatic phenomena, e.g., electrophoresis, do not necessarily involve the use of non-polar solvent systems. Thus an electrostatic method using water as the carrier system in electrostatography is shown in U.S. Letters Pat. No.

3,425,829, issued Feb. 4, 1969. Other suitable solvent system, by way of example, i.e., solvent systems other than petroleum fractions and water, include alcohols, e.g., those having 1 to 6 carbon atoms, such as ethylene glycol; ethers, including ethyl isobutyl ether, methyl isopropyl ether, the (C₁-C₄) alkyl mono ethers of ethylene glycol, and dioxane; ketones, including acetone, methyl ethyl ketone, methyl isopropyl ketone, and ethyl isobutyl ketones; esters, including ethyl acetate, amyl acetate, butyl propionate, and the acetates of the mono- (C₁-C₄) alkyl ethers of ethylene glycol; and halogenated hydrocarbons, such as chloroform, ethylene dichloride, monochloro benzene and certain Freons.

After selection of the solvent system a polymeric backbone molecule is chosen, which is solvated by the selected solvent system, i.e., which is fully soluble to the limit of its solubility. Next a graft or block polymerization or copolymerization is carried out in such a manner, hereinafter described, that non-solvated polymeric chains, which is to say, polymeric chains which are not solvated by the chosen solvent system, are created in the solvent system and are chemically joined with, i.e., to, the solvated polymeric backbone molecule. For the purpose of the present invention, the mechanism by which the chains are created and chemically joined is not of critical importance. For example, the chains first can be formed and then grafted onto the polymeric backbone molecule or a molecule of a grafting monomer can be first reacted with the polymeric backbone molecule and subsequently this first monomer can be polymerized with the other grafting monomers present in the solvent system.

The non-solvated polymeric moiety, i.e., fraction or chains, originates as a monomer which usually and preferably is solvated by the solvent system for convenience in carrying out the reaction and to minimize the time required for the reaction and also to eliminate the need for solublizers or multi-solvent systems. However, as the reaction for the formation of the chains proceeds the addition to the backbone polymer, which is to say, the newly formed chains, become progressively non-solvated and eventually becomes a non-solvated moiety (portion) which constitutes a dispersed phase, this, despite the fact that the polymeric backbone still is solvated by the solvent system. It is interesting to observe that the reaction as it takes place initially causes a transformation of the clear solution of the solvated backbone polymer and of the solvated monomer first into a slightly hazy stage and then becomes more turbid as the minutes pass until ultimately a latex is formed.

It is also possible to use a reverse process in which a non-solvated polymeric backbone is partially solvated by graft or block polymerization.

As mentioned previously, the largest present-day commercial use for liquid toners is in electrostatography such as is used in the so-called "liquid" xerographic copying machines. The solvent system used in liquid toners for such purpose is usually a petroleum fraction such as described heretofore and, hence, in detailing various process steps in the manufacture of the complex molecule this particular solvent system will be employed, although it is understood that the invention is not limited thereto and can employ any solvent system whatsoever.

Assuming, then, that the solvent system is a petroleum fraction, a polymeric backbone material is selected which is solvated by such petroleum fraction. A popularly employed petroleum fraction is odorless mineral spirits (hereinafter OMS). There are many polymeric materials which are solvated by OMS. These include, e.g., polymeric materials derived from natural sources such as crepe rubber; refined oxidized linseed oil and degraded rubber, and synthetic polymers such as alkyd resins; polyisobutylene; polybutadiene; polyisoprene; polyisobornyl methacrylate; acrylic polymers of long chain esters of acrylic or methacrylic acid such as stearyl, lauryl, oodecyl, octyl, 2-ethylhexyl and hexyl; butyl esters of acrylic or methacrylic acids; polymeric vinyl esters of long chain acids such as vinyl stearate, vinyl laurate, vinyl palmitate and vinyl myristate; polymeric vinyl alkyl ethers, including poly (vinyl ethyl ether) sold under the trademark Bakelite EDBM by Union Carbide Corp., poly (vinyl isopropyl ether), poly (vinyl isobutyl ether) and poly (vinyl n-butyl ether). As can be seen from the examples given, the polymers chosen have a structure similar to that of the solvent which is going to solvate them, i.e., the polymers and the solvent system have a similar degree of polarity. As long as this similar polarity is maintained, copolymers, e.g., lauryl methacrylate-butyl acrylate, t-octyl methacrylate-butyl methacrylate, lauryl methacrylate-glycidyl methacrylate, 2-ethyl hexyl acrylate-acrylic acid, isodecyl methacrylate-diethylaminoethyl methacrylate and vinyl toluene-butadiene; terpolymers, e.g., lauryl methacrylate-isodecyl methacrylate-methyl methacrylate, stearyl methacrylate-cyclohexyl acrylate-methacrylic acid, octyl acrylate-crotonic acid-dodecyl methacrylate, glycidyl methacrylate-stearyl methacrylate-lauryl methacrylate, lauryl methacrylate-octyl methacrylate-glycidyl methacrylate and isodecyl methacrylate-stearyl methacrylate-acrylic acid; and tetrapolymers, e.g., N-vinyl pyrrolidone-butyl acrylate-lauryl methacrylate-stearyl methacrylate and acrylic acid-stearyl acrylate-methyl methacrylate-isodecyl acrylate, may be used, as well as block and graft copolymers, block and graft terpolymers, block and graft tetrapolymers and multi-type monomer/polymers in general as the backbone structure.

If desired, the backbone structure with or without added polymers chains can be created in a solvent other than that in which it is ultimately to be used, i.e., in a solvent other than the solvent system of the liquid toner. The original solvent in which the backbone structure with or without added chains is created can either be extracted or it can be part of a multi-solvent system in the liquid toner. Many monomers which it might be desirable to employ in building a backbone structure are not sufficiently solvated by OMS or other solvent system of the liquid toner to enable the polymerization of the desired structure to be effected in OMS. In such a case, a copolymerization utilizing such

insufficiently solvated monomers may be carried out in a solvent of higher K.B. number with another monomer which is solvated by OMS, as long as the resultant copolymer contains enough of the second monomer so that the backbone can be solvated by OMS. Such a copolymerization, for example, could be carried out in benzene, the resulting copolymer precipitated by the addition of methanol, freed from solvent, and dissolved in OMS to function as the backbone during the subsequent graft or block polymerization or graft or block copolymerization.

The discussion above of synthetic polymeric materials suitable for use as the backbone, also often herein-after sometimes referred to as the "precursor", in an OMS-based electrostatographic toner system is not limited to addition polymers; synthetic condensation polymers can also serve as the backbone or precursor in this system as long as they can be solvated by the chosen solvent medium, e.g., the self-condensation polymer of 12-hydroxystearic acid.

Inasmuch as the present invention is not limited to any particular solvent system, there is no limitation on the monomers that can be used to fabricate the polymeric constituents of the system. In the particular system being discussed, however, that based on OMS, the following list of backbone polymers is exemplificative but not exclusive:

a. the homopolymers of the C_4 - C_{22} esters of acrylic and methacrylic acid, such as polyhexyl methacrylate and acrylate, polyisodecyl methacrylate and acrylate, polylauryl methacrylate and acrylate, polytetradecyl methacrylate and acrylate, and polystearyl methacrylate and acrylate, all in the molecular weight range of about 10^3 to about 10^6 , but preferably not smaller than 10^4 ;

b. copolymers, with each other, of any of the above monomers used to form the homopolymers under (a), and also with the methyl, ethyl, isopropyl and propyl esters of acrylic and methacrylic acid, provided that the ratios of non-solvated to solvated monomers are kept in a proportion such as to insure solvation of the resulting copolymer by OMS;

c. copolymers of the above mentioned methacrylic and acrylic acid esters with monomers containing other functional groups as, for example, acrylic acid, methacrylic acid, crotonic acid, maleic acid, atropic acid, fumaric acid, itaconic acid, citraconic acid, acrylic anhydride, methacrylic anhydride, maleic anhydride, acryloyl chloride, methacryloyl chloride, acrylonitrile, methacrylonitrile, acrylamide and derivatives thereof, methacrylamide and derivatives thereof, hydroxyethyl methacrylate and acrylate, hydroxypropyl methacrylate and acrylate, dimethylaminomethyl methacrylate and acrylate, dimethylaminoethyl methacrylate and acrylate, dimethylaminoethyl methacrylate and acrylate, diethylaminoethyl methacrylate and acrylate, t-butylaminoethyl methacrylate and acrylate, allyl alcohol and derivatives thereof, cinnamic acid and derivatives thereof, styrene and derivatives thereof, methallyl alcohol and derivatives thereof, propargyl alcohol and derivatives thereof, indene and derivatives thereof, norbornene and derivatives thereof, vinyl ethers, vinyl esters and other vinyl derivatives, glycidyl methacrylate and acrylate, mono- and dimethyl maleate, mono- and dimethyl fumarate, mono- and diethyl maleate and mono- and diethyl fumarate;

d. homopolymers of olefins such as polybutadiene, polyisoprene, polyisobutylene, and copolymers of these

monomers with any of the monomers listed above consistent with the solvation limitation as described under (b);

- e. terpolymers and tetrapolymers of the above;
- f. polycarbonates, polyamides, polyurethanes and epoxies.

With the backbone, i.e., precursor, chosen, there are added on to this backbone polymeric chains of a different degree of polarity from that of the solvent so that these chains, although grafted on or block polymerized to the solvated backbone, will themselves be non-solvated by the solvent system and, hence, form a dispersed phase. This addition of such chains is carried out via either a block or graft polymerization as just noted. Suitable monomers which form polymers that are too polar to be solvated by the GMS solvent medium are vinyl acetate, methyl acrylate and methacrylate, ethyl acrylate and methacrylate, propyl acrylate and methacrylate, isopropyl acrylate and methacrylate, hydroxy ethyl acrylate and methacrylate, hydroxy propyl acrylate and methacrylate, acrylonitrile, methacrylonitrile, acrylamide, methacrylamide, acrylic acid and anhydride, methacrylic acid and anhydride, mono methyl maleate, mono methyl fumarate, mono ethyl maleate, mono ethyl fumarate, styrene, vinyl toluene, maleic acid and anhydride and crotonic acid and its anhydride. The invention is not limited to homopolymers in this further polymerization procedure; copolymers and terpolymers or polymers of greater degrees of complexity, but of the proper polarity, could be joined to the chosen solvated backbone structure to form the latex.

When a grafting procedure is chosen for the latex forming step, and there are no ethylenic or other unsaturated bonds available in the backbone for accepting the graft, polymeric chains can be grafted onto a saturated backbone, nevertheless, through the use of activating methods known to those skilled in the art. This method, however, although useful, leads to a haphazard activation by the initiator employed of a site or sites in the backbone molecule which subsequently serve to initiate the polymerization of the grafting monomer. A preferred method, rather than haphazard activation, is to construct the backbone molecule in such a way as to produce ethylenically unsaturated double bonds or other unsaturated bonds containing pendant moieties to serve as sites to be activated by the initiator for in situ graft polymerization. Thus, there may be employed an OMS solvated backbone molecule consisting of a copolymer of stearyl methacrylate-glycidyl methacrylate of the proper (27:1) monomer ratio and molecular weight, e.g., 10,000 to 150,000. Methacrylic acid can be reacted with this polymer in the presence of a polymerization inhibitor to provide ethylenically unsaturated double bond containing sites through an esterification reaction for activation and subsequent in situ polymerization or copolymerization. In such a manner, precursors for a graft polymerization or copolymerization can be made. The term "precursor" as used herein denotes a backbone such as described, as well as a treated (activated) backbone, which is to be used as the base for reaction to form a latex.

Many different reactions can be utilized to introduce these ethylenically unsaturated double bond containing pendant groups into the precursor. If the comonomer of the backbone chain is called Monomer 1 (such "comonomer" is at least one of two monomers which forms the backbone chain and which is present in a mi-

nority proportion by weight and which includes an unsaturated bond before copolymerization, said bond having been reacted in the formation of the copolymer but still contains a reactive group) and the precursor monomer is called Monomer 2 (the precursor is specifically selected to be reactive with the reactive group of the comonomer), the following are illustrative examples:

Monomer 1	Monomer 2
10 Glycidyl methacrylate or acrylate	Acrylic acid Methacrylic acid Maleic acid Fumaric acid Atropic acid Allylamine Vinyl amine
15 Acryloyl or methacryloyl chloride	Hydroxyethyl methacrylate and acrylate Hydroxypropyl methacrylate and acrylate Acrylamide Methacrylamide Allyl alcohol Allylamine Vinyl amine
20 Acrylic acid Methacrylic acid Maleic acid Crotonic acid Alkyl hydrogen maleates Alkyl hydrogen fumarates	Vinyl pyridines Glycidyl methacrylate Vinylamine Allylamine Dialkylaminoalkyl methacrylates and acrylates
25 Vinyl isocyanate	Allylamine Vinylamine Methacrylyl acetone
30 Cyanomethylacrylate	Vinylamine Allylamine Allylamine Vinylamine Allyl alcohol Hydroxyalkyl methacrylates Glycidyl methacrylate Vinylamine Allylamine
35 Methacrylic anhydride Acrylic anhydride Maleic anhydride	Hydroxyalkyl methacrylates Allyl alcohol N-hydroxymethyl methacrylamides
40 Vinyl sulphonic acid Vinyl phosphoric acid	Alkoxyethyl methacrylamides

The reverse reactions can also be utilized, i.e., Monomer 2 can be copolymerized into the backbone and subsequently condensed with Monomer 1 to create the precursor.

With the precursor formed, the latex is prepared by carrying out, in a liquid system wherein the precursor or additional fraction (moiety) is fully solvated and the other fraction (moiety) not fully solvated, the polymerization of the monomer or comonomers chosen for the additional fraction which preferably is the dispersed phase in the presence of and in conjunction with the precursor. In the preferred form of the invention, the monomer or monomers chosen polymerize to a material which is nonsolvated by the solvent system employed. For example, in an OMS-based system using the stearyl methacrylate-glycidyl methacrylate-methacrylic acid precursor, typical useful monomers for the additional fraction include methyl methacrylate, methylacrylate, ethyl methacrylate, ethyl acrylate, isopropyl methacrylate, styrene, vinyl acetate, vinyl chloride, vinyl toluene, acrylonitrile and methacrylonitrile, as homopolymers or copolymers, or any one or more of the above with maleic anhydride, crotonic acid, acrylic acid, mono methyl maleate, mono methyl fumarate, mono ethyl maleate, mono ethyl fumarate, methacrylic acid, dimethylaminomethyl methacrylate, or terpolymers or tetrapolymers of any of the foregoing. When

this polymerization is carried out, part of the monomer polymerizes with the precursor molecule (solvated backbone) to form a graft copolymer which is one form of complex tailored molecule embodying the invention, and this serves to stabilize any disperse polymer particles which are not grafted.

It will be appreciated that the dispersed phase which, in principle, is the non-solvated moiety of the complex amphipathic resin molecule, also may include dispersed non-grafted non-solvated polymer particles. Although the latter are not particularly desirable by virtue of their non-solvation, they are aggregatable and, moreover, are able to behave electrophoretically so that they are capable of being selectively attracted to differentially electrostatically charged areas, whereby to form a graphic representation by electrostatography.

With a latex of the foregoing character constituting the complex tailored amphipathic resin molecule as thus far described, the fixative (substrate bonding) and dispersant functions are combined into a single molecule which will behave properly in an electrostatographic system. That is to say, this molecule, of which there are a great number in any particular liquid toner, will be capable of charge direction and fixation and yet will not, because of the solvated moiety, tend to settle so that it has a "built-in" dispersing ability. Moreover, because, in effect, the molecule includes both an equivalent of a fixative agent and an equivalent of a dispersing agent in a single molecule, the two will be consumed (depleted) at fixed rates, depending upon their proportions in the molecule. Hence, when they are to be replenished, they do not have to be replenished at different rates to bring back the original optimum conditions, nor will there be a deviation from original optimum conditions and proportions because of a differential rate of depletion. Thereby, at least as to the dispersant and fixative functions, a substantial improvement over the prior art has been obtained.

Of course, this complex tailored molecule, together with the solvent system, is not capable, by itself, of use as a liquid toner, that is to say, to form a visible selective deposition on a differentially electrostatically charged substrate. It is additionally necessary for the liquid toner to contain a color ranging from black to white through all of the various hues. Phrased differently, it is necessary to color the suspended latex particles so that when they are preferentially attracted to differentially electrostatically charged regions of a substrate and deposited thereon, the film left by the deposit ("film" is here used in a sense not of a broad continuous layer but, rather, of a coating which may cover only a physically small portion of an area and may have any type of peripheral configuration depending upon the image that is to be produced) will likewise be colored so that they can be readily visible and also, if desired, so that a specific color can be created.

One way of imparting the color is by using either pigments or dyes added to the latex and physically dispersing them therein as by ball milling or high shear mixing.

The pigment employed can be any one of the many now known to the art in connection with liquid electrostatographic developers. As is well known, these pigments essentially constitute very fine solid particles the size of which is in the submicron range and which are opaque en masse. They are insoluble in the liquid system. So many different kinds and species of pigments are known that only typical representative examples will be mentioned. These are: powdered metals, e.g.,

powdered aluminum; powdered metal oxides, e.g., powdered magnetic iron oxide, e.g., powdered metal salts, e.g., powdered cadmium selenide (CdSe), powdered lead iodide (PbI₂), powdered lead chromate (PbCrO₄); Acetamine Black CBS (Dupont)*; Nigrosine Base No. 424 (Dupont) (50415 B) **; Hansa Yellow G (General Aniline) (11680); Spirit Nigrosine SSB (National Aniline) (50415); Rubanox Red CP-1495 (Sherwin-Williams) (15630); Raven 11 (Columbian Carbon) carbon black aggregates with a particle size of about 25 μ ; and chrome green.

*material in first parentheses indicates name of manufacturer. **material in second parentheses indicates color index number.

When the dispersed phase is colored by pigment, such preferably are non-reactive with the amphipathic polymer. It is believed that pigment particles are held to the non-solvated latex moiety by second order forces only, i.e., are thus held to the dispersed phase of the complex amphipathic resin molecule. It has been observed that graphic representations, e.g., electrostatographic images, formed by the use of the system above described, that is to say, with the use of liquid toners of the invention, are smear-resistant to a very substantial degree and considerably superior in this and other respects (e.g., clarity of background and easier replenishment) to liquid toners commercially available. However, they are not smear-proof. Nevertheless, liquid toners embodying pigment particles held in the foregoing manner have a definite commercial utility. For instance, they can be used as liquid toners to lay down a phosphor layer in color television tubes.

In a preferred form of the invention, the images formed by the liquid toner are smear-proof and this is accomplished, as will later be pointed out, by employing pigments or dyes which are chemically bonded to the latex, that is to say, which become chemically bonded to and are part of the complex molecule. The chemical bonding can be to the precursor before the graft or block polymerization of the added chains or it can be to the chains added by graft or block polymerization.

As to dyes, as distinguished from pigments, these may be used to color the specific complex amphipathic resin polymer molecule and specifically to color the dispersed non-solvated phase thereof by being held thereto by second order or surface adsorption forces or the dyes can be chemically reacted with the complex tailored molecule, either after its formation, or to the precursor, or to the chain as it is being or after it has been grafted or block polymerized.

The dyes are incorporated in a liquid toner by second order or surface adsorption forces, as by heating the latex and dye together for a sufficient time, for example, one to twelve hours. One type of example of such dyes is dispersed dyes for dyeing polyester and copolymers of acrylonitrile and vinyl chloride where the dispersed phase is a polyester or a copolymer of acrylonitrile and vinyl chloride. Such dyes include: Latyl Orange 3R (Dupont) (C.I. Disperse Orange 26); Calcosperse Yellow GL (American Cyanamid) (C.I. Disperse Yellow 57); Calcosperse Blue B (American Cyanamid) (C.I. Disperse Blue 77); Foron Blue BGL (Sandoz Inc.) (C.I. Disperse Blue 73); Latyl Brown MS (Dupont) (C.I. Disperse Brown 2); and Latyl Violet BN (Dupont) (C.I. Violet 27). Other examples of such dyes are basic dyes for polyacrylics, where the dispersed phase is a polyacrylic. Typical of such dyes are: Sevron Blue BGL (Dupont) (C.I. Basic Blue 35); Sev-

ron Brilliant Red 3B (Dupont) (C.I. Basic Violet 15); Deorlene Brilliant Red 3B (Ciba) (C.I. Basic Red 26); Calcozine Arcylic Blue G (American Cyanamid) (C.I. Basic Blue 38); Astrazon Yellow Brown GGL (Farbenfabriken Bayer) (C.I. Basic Orange 30); and Astrazon Red 5BL (Farbenfabriken Bayer) (C.I. Basic Red 24).

The use of a dye held by second order or surface adsorption forces is suitable for many purposes because it has a good degree of smear-resistance and is superior to present-day commercially available liquid toners in such respect. However, as in the case of similarly held pigments, the deposit on a surface is not smear-proof. But such a dye-colored liquid toner has an excellent commercial useage where the areas upon which deposits are made are not exposed to abrasion, i.e., actions which cannot result in smearing, e.g., a phosphor deposit on the inside face of a color television tube, and, indeed, it is acceptable for graphic copy work.

Nevertheless, a better approach and one which is preferred in a more sophisticated form of the present invention is to create a dispersed (non-solvated) phase of a copolymer containing reactive groups which will react with reactive groups of a chromophoric nature, for example, a dispersed phase of a copolymer containing basic groups which can be reacted with acid dyes. An example of a dispersed phase of a latex which can be used in the foregoing manner is a terpolymer of acrylonitrile, 2-methyl-5-vinyl pyridine and vinyl acetate. Such terpolymer can be reaction dyed with dyes containing acid groups of which examples are: Pontacyl Brilliant Blue A (Dupont) (C.I. Acid Blue 7); Calcocid Brilliant Blue FFR (American Cyanamid) (C.I. Acid Blue 104); Femazo Brown N (General Aniline) (C.I. Acid Brown 14); Crocein Scarlet N (Dupont) (C.I. Red 73); Oxanal Yellow I (Ciba) (C.I. Acid Yellow 63); and Benzyl Black 4BN (Ciba) (C.I. Black 26A).

Such a complex tailored molecule is tri-functional. It contains not only the dispersant and fixative functions but also the coloring functions, whereby the single sophisticated molecule has a fixed depletion rate for all three of these functions and a liquid toner containing this type of molecule can be replenished with a toner containing identical molecules. Moreover, the liquid toner has an essentially mono-dispersed phase, i.e., a small range of variation of particle size. Thereby, the operating bath made up of this toner will always operate with maximum efficiency.

It will be appreciated that a bath with a liquid solvent system and the fixative/dispersant/color functions in a single molecule omits only one function, to wit, that of charge direction. Accordingly, the constitution of the bath is now far simpler; its operation is far more efficient; and its replenishment is much easier. Furthermore, because of the mono-dispersed phase, the toner yields excellent resolution.

An alternate method of creating the more sophisticated complex tri-functional amphipathic resin molecule which embodies the aforesaid three functions of fixing, dispersing and coloring is to create a dispersed phase of a copolymer containing acid groups which then are reacted with basic dyes (instead of with the aforesaid acid dyes). An example of a dispersed phase of such a latex is a copolymer of vinyl acetate-maleic acid. This is dyeable with dyes containing basic groups of which examples are: Magneta (C.I. Solvent Red 41, C.I. No. 42510B), Crystal Violet (C.I. Solvent Violet 9, C.I. No. 42555B), Bismarck Brown (C.I. Solvent Brown 12, C.I. No. 21010B), Victoria Blue BA (C.I.

Solvent Blue 4, C.I. No. 44045B), Victoria Blue R (C.I. Solvent Blue 6, C.I. No. 44040R), Victoria Blue 4R (C.I. Solvent Blue 2, C.I. No. 42563B), Copying Black SK (C.I. No. 11975), Janus Green B (C.I. No. 11050), Auramine O (C.I. Solvent Yellow 34, C.I. No. 41000B), Victoria Green (C.I. Solvent Green 1, C.I. No. 42000B), and Rhodamine (C.I. Solvent Red 49, C.I. No. 45170B).

Still another method of creating a tri-functional complex tailored amphipathic resin molecule pursuant to the invention by virtue of a chemical reaction for bonding the color agent to the block or graft modified precursor is to create a dispersed phase of a copolymer containing electron acceptor groups, for example, maleic acid or crotonic acid which are Lewis acids and which are then reacted with color precursors that are well known in the art. An example of this latter tri-functional sophisticated complex molecule is a terpolymer of maleic anhydride-vinyl acetate-styrene (on a solvated backbone) and reacted with a color precursor such for instance as bis (p-dimethylaminophenyl)-benzotriazyl methane. A liquid toner embodying the foregoing complex molecule will produce a deep blue colored deposit.

Where the pigment or dye is reacted with the added groups in the dispersed phase, the amount of pigment employed can fluctuate from as low as 5 percent to a theoretical 100% of the calculated stoichiometric amount. Nevertheless, it is preferred to have the amount of dye or pigment thus incorporated vary between about 10 and 50 percent of the stoichiometric amount, with best results having been obtained at about 25 percent of the stoichiometric figure.

There is yet another way, in accordance with the present invention, for coloring latexes, i.e., liquid toners. This is to color the precursor itself, which is to say, the backbone that is the solvated phase rather than to color the dispersed unsolvated phase. Although there could be used for coloring the precursor some of the methods recited above to color the dispersed phase by chemical reaction or by second order bonds or surface adsorption or even by chemical reactions of chromophores with the precursor, a highly preferred method is to employ a dye which is copolymerized into the precursor itself, that is to say, the solvated backbone, before the backbone is grafted or block polymerized with the non-solvated moieties (chains). An example of such a process is set forth below (EXAMPLE VIII) along with many other examples of methods of manufacturing the complex amphipathic resin molecule of the present invention.

It should be observed, moreover, that, if desired, both the dispersed phase and the solvated precursor can be dyed by any of the manners above discussed in detail.

As thus far described, there has been provided a stable latex which constitutes practically all of the necessary ingredients of a liquid toner, these including the liquid solvent system with the complex amphipathic resin molecule having solvated and non-solvated moieties and which is tri-functional as to the fixative, dispersant and colorant or includes a separate (non-reacted) color agent. It still is, nevertheless, extremely desirable to include in the liquid toner a charge director or directors, the same adding greatly to the depth of color obtained in electrostatographic development and aiding in contrast. Hence, pursuant to the present invention there preferably is included in the liquid toner

as a component over and above the solvent system, the complex molecule and a separate colorant, if one is not included as a moiety of the complex molecule, a charge director in the proper concentration to permit the liquid toner to function effectively for the particular use intended. In electrostatographic development a charge director present in a suitable concentration is to all intents and purposes a necessity.

Inasmuch as the present invention is capable of functioning with a wide variety of solvent systems ranging from non-polar to polar, and since there are a wide variety of charge directors which are known to the art, the present specification does not hereinbelow set forth an all-inclusive list of such materials. Indeed, even restricting the solvent to a petroleum fraction, specifically OMS, it would not be practical within the confines of this specification to list every one of the known charge directors.

The charge directors in a conventional liquid electrostatographic toner serve several purposes. In general, they are adsorbed by the pigment particles and seem to act as bridges between the "ultimate particle size" particles leading to an agglomeration or partial flocculation of these very tiny particles to form the aggregates which ultimately are deposited on an electrostatically charged substrate such as the patterned electrostatically charged image area of an electrostatic latent image, or on the non-image area in the case of a reverse toner. The charge directors also appear to create a molecular environment about these aggregates which is responsive either via electrostatic and/or polarization effects to the influence of the electric field. They also are able to modify the conductance of the continuous phase which facilitates the action of the field of an electrostatic latent image to either attract or repel the suspended aggregates.

In the liquid toner system of the present invention, since the particles that have been created are virtually monodispersed and remain this way because of the entropic repulsion of the polymeric precursor chains, the charge directors present in the new system probably have only the two-fold purpose of creating the correct molecular environment around the particles and of modifying the conductance of the continuous phase. In other words, they are not useful nor do they need to be of any assistance in connection with flocculation (aggregation).

The various charge directors which are conventionally employed in the commercial and patented liquid electrostatographic toners for the development of electrostatographic images in office copy machines and the like, are useful in the unique toner of the present invention. Examples thereof are:

Aerosol OT which is di-2-ethylhexyl sodium sulfosuccinate;

Aerosol TR which is di-tridecyl sodium sulfosuccinate;

the aluminum, chromium, zinc and calcium salts of 3, 5-dialkylsalicylic acid, wherein the alkyl group is propyl, isopropyl, butyl, isobutyl, tertiary butyl, amyl, isoamyl and other alkyl groups up to C-18;

the aluminum, chromium, zinc and calcium salts of dialkyl gamma-resorcylic acid, wherein the alkyl is as above;

the isopropylamine salt of dodecylbenzene sulfonic acid;

aluminum, vanadium and tin dresinates (the metal dresinates are prepared by adding a solution of the

metal sulfate to a solution of the sodium salt of Dresinate 731 manufactured by Hercules Powder Co.);

aluminum stearate;

cobalt, iron and manganese octoates;

5 OLOA 1200 which is a product of the Oronite Division of California Chemical Co., the same being a partially imidized polyamine with lubricating-oil-soluble polyisobutylene chains and free secondary amines, its specifications are: gravity at 60°F API 22.9, specific gravity 0.92, flash point by the Cleveland open cup method, 425°F, viscosity at 210°F, 400 SSU, color (ASTM D-1500) L55D, nitrogen, percentage by weight 2.0, and alkalinity value, (SM-205-15) 43;

soya bean lecithin;

15 an aluminum salt of 50-50 by weight mixture of the mono- and di- 2 ethylhexyl esters of phosphoric acid; and

Alkanol DOA which is a product of E. I. duPont de Nemours & Co., Inc. This product is a viscous light 20 amber colored liquid composed 50 percent by weight of a terpolymer in kerosene. The terpolymer consists of 50 percent by weight octadecenyl methacrylate, 40 parts by weight styrene and 10 parts by weight diethylaminoethyl methacrylate. The specific gravity of the product at 77°F is 0.888. Its acid number (milligrams KOH/gram of sample) is 0.2. Its total monomer content is 15.5 percent maximum by weight. Its basic nitrogen content is 0.40 percent $\pm$ 0.03 percent by weight. Its base number (equivalent to milligrams KOH/gram of sample) is 13.8.

Where charge directors are used they preferably are soluble in the liquid solvent system (aluminum stearate is the sole insoluble one) and the charge director employed (more than one can be employed if desired) is a material which when present in the latex, i.e., dissolved 35 in the latex solvent system, will reduce the resistivity of the latex solvent system from 10^{14} to no less than 2×10^9 ohm cms. and desirably between 10^{13} to 10^{10} ohm cms. and preferably between 2×10^{12} and 10^{11} ohm cms. It is pertinent to observe that toner resistivity is not per se the sole criterion of acceptable prints. Frequently where two different charge directors adjust a toner resistivity to the same value the prints obtained using the two different toners will not be equally acceptable.

The amounts of the different solid constituents of the liquid toner (amphipathic molecule, optimally a coloring material, and a charge director) are capable of extremely wide variation, indeed, so wide that assigning specific figures thereto of the extreme ranges which function in accordance with the invention is largely meaningless. For example, the amounts will vary with the type of machine, climate, machine seeds, types of paper and experience of the operator, to mention but a few. Also, particularly in the case of the coloring material, the amounts will vary with the intensity of the dye or pigment and the desired degree of intensity of the image. Generally speaking, moreover, the amounts of the individual solids compounds will increase or decrease together, although not in strict proportion. Bearing all of this in mind and in order to assist workers in the art in the preparation of toners embodying the present invention, the following represent approximately maximum and minimum amounts of the various solids constituents per liter of liquid toner.

For the complex amphipathic molecule where the same includes a dye or pigment either chemically reacted therewith or bonded thereto or affiliated there-

with by surface adsorption forces from about 0.03 g. to about 30 g.

For the complex amphipathic molecule where the same does not include a chromophore reacted or associated therewith from about 0.03 g. to about 30 g.

For the color agent where the same is not reacted or bound to the complex amphipathic molecule from about 0.03 g. to about 30 g.

For the charge director from about 1×10^{-6} g. to about 10 g.

Examples of different specific embodiments of the invention follow:

The first nine examples are examples of precursors, i.e., examples of the formation of the backbone, that is to say, the spine, of the amphipathic molecule with which a subsequent reaction will later be described in further examples which deal with the formation of the latices from the precursors and toners from the latices.

EXAMPLE I

In a clean dry 8 oz. glass jar is placed 100 gs. of 2-ethylhexyl-acrylate and 1 g. of AZBN (azobisisobutyronitrile), a polymerization initiator. The jar is placed in a water bath maintained at $75^{\circ} \pm 2^{\circ}\text{C}$. After about 30 minutes an exothermic polymerization takes place. The temperature reaches a maximum of 120°C . in about 5 minutes after the start of the exotherm. After it cools down to 90°C . the jar is removed from the water bath loosely covered and placed in a hot air oven at 90°C . overnight to complete the polymerization. The product is a nearly water-white heavy syrup.

EXAMPLE II

Four hundred grams of petroleum ether (b.p. 90° – 120°C) is placed in a 1 liter reaction flask equipped with a stirrer, a thermometer, a reflux condenser, and a dropping funnel and heated to a gentle reflux at atmospheric pressure. A solution of 1.2 g. AZBN in 200 g. of 2-ethylhexyl-acrylate and 6 g. of glycidyl methacrylate is placed in the dropping funnel and allowed to drip into the reflux stream at such a rate that the addition takes 3 hrs. The mixture is refluxed at atmospheric pressure for an additional 2 hrs. at which time 4 g. of acrylic acid, 0.14 g. of 2, 6-di-tertiary butyl-phenol and 1 g. of lauryl dimethyl amine is added. The mixture is refluxed at atmospheric pressure for 12 more hours under a nitrogen blanket to esterify ca. 25 percent of the glycidyl rings of the copolymer. The product is a straw-colored somewhat viscous liquid.

EXAMPLE III

In a 500 ml. resin reactor equipped with a stirrer, a thermometer, a reflux condenser and a dropping funnel is placed 250 gms. of Isopar E. The solvent is heated to $93^{\circ} \pm 1^{\circ}\text{C}$. and 250 gs. of 2-ethylhexyl acrylate containing 1.5 gs. of AZBN is added dropwise to the hot solvent over a period of 3 hrs. The mixture is maintained at $93^{\circ} \pm 1^{\circ}\text{C}$. for 3 additional hours to complete polymerization. All reactions take place in the reactor at atmospheric pressure. The product is a slightly viscous straw-colored liquid.

EXAMPLE IV

In a 1 liter reaction flask equipped with a stirrer, a thermometer and a reflux condenser is placed 400 gs. of petroleum ether (b.p. 90° – 120°C .) and the same is then heated at atmospheric pressure to a moderate rate of reflux. A solution is made of 194 gs. lauryl metha-

crylate, 6.0 gs. of glycidyl methacrylate and 3.0 gs. of benzoyl peroxide paste (60 percent by wt. in dioctyl phthalate) and placed in a 250 ml. dropping funnel attached to the reflux condenser. The monomer mixture is allowed to drip into the refluxing solvent at such a rate that it requires 3 hrs. for the total amount to be added. After refluxing 40 minutes at atmospheric pressure beyond the final addition of monomer, 0.5 gs. of lauryl dimethyl amine is added and the refluxing is continued at atmospheric pressure for another hour. Then 0.1 g. hydroquinone and 3.0 gs. methacrylic acid are added and refluxing continued under a nitrogen blanket until ca. 52 percent esterification of the glycidyl groups is effected (about 16 hours). The resulting product is a slightly viscous straw-colored liquid.

EXAMPLE V

EXAMPLE IV is repeated except that the final refluxing is concluded when ca. 25 percent esterification of the glycidyl groups has been effected.

EXAMPLE VI

In a 5 liter jacketed glass reactor open to the atmosphere and equipped with a stirrer, a thermometer, a nitrogen bubbler and a reflux condenser is placed 2400 gs. of Isopar G. The solvent is heated to $110^{\circ} \pm 1^{\circ}\text{C}$. by circulating hot triethylene glycol through the jacket. The temperature of the glycol is controlled by a proportional heating unit with its temperature sensor in a reservoir of the heating fluid from which the hot liquid is pumped to the reactor and subsequently returned to the reservoir for further heating. A three-way valve arrangement allows the glycol heating system to be isolated from the jacketed reactor so that cold water can be immediately supplied to the jacketed reactor to keep the temperature constant during the polymerization exotherm when necessary. When the solvent reaches the foregoing temperature, a mixture of 1035.7 gs. isodecyl methacrylate, 36.0 gs. glycidyl methacrylate and 18.0 gs. Luperco ANS-50 (a paste consisting of 50 percent benzoyl peroxide by weight in dioctyl phthalate) is added at a constant rate over a 3 hr. period through a dropping funnel attached to the condenser. After all of the monomer solution has been added, the reaction mixture is held at $110^{\circ} \pm 1^{\circ}\text{C}$. for another 30 min. Then 3.0 gs. lauryl dimethyl amine is added and the reaction mixture again held at said temperature for 1 hr. At this point 0.6 gs. hydroquinone is added and the nitrogen bubbler is started to provide a nitrogen blanket during the esterification. Then 18.0 gs. of methacrylic acid is added and the reaction temperature is maintained until an acid drop indicates that 25 percent of the glycidyl rings have been esterified (ca. 8 hrs.). The product that results is a slightly viscous straw-colored liquid.

EXAMPLE VII

Using the same apparatus as described in EXAMPLE VI, 1440 gs. of Isopar G is warmed to $110^{\circ} \pm 1^{\circ}\text{C}$. To this hot solvent, a solution of 1278.6 gs. stearyl methacrylate, 32.4 gs. glycidyl methacrylate, and 16.2 gs. Luperco ANS 50 in 720 gs. of Isopar G is added through a dropping funnel attached to the condenser over a 3 hr. period, the temperature being maintained at $110^{\circ} \pm 1^{\circ}\text{C}$. After all of the monomer solution has been added, the reaction mixture is held at $110^{\circ} \pm 1^{\circ}\text{C}$. for another 40 mins. Then 2.8 gs. lauryl dimethyl amine is added and the reaction mixture again held at said

temperature for 1 hour. At this point 0.54 gs. hydroquinone is added and the nitrogen bubbler is started to provide a nitrogen blanket during the esterification. Then 16.2 gs. methacrylic acid is added and the reaction temperature is maintained until an acid drop indicates that 24 percent of the glycidyl rings have been esterified (ca. 7 hrs.). The product is a slightly viscous straw-colored liquid.

EXAMPLE VIII

In a 500 ml. 3-neck round-bottom reaction flask open to the atmosphere and equipped with a stirrer, a thermometer, a thermocouple for a thermoregulator and a reflux condenser, is placed 197.8 g. Isopar G. The solvent is warmed to $110^{\circ} \pm 1^{\circ}\text{C}$. with stirring. A mixture of 96.0 g. lauryl methacrylate, 3.0 g. glycidyl methacrylate, 0.74 gs. benzoyl peroxide (99%), 50 mls. of benzene and 5.0 gs. of p-phenylazoacrylanilide is prepared by stirring on a magnetic mixer for 30 minutes at room temperature. Most but not all of the p-phenylazoacrylanilide dissolves. This mixture is added in 5 ml. increments at 5 min. intervals over a period of 3 hrs. to the solvent in the flask. The mixture is kept well stirred so that each addition will be identical in composition. After the last addition, the mixture is allowed to react at $110^{\circ} \pm 1^{\circ}\text{C}$. for 45 minutes and then 0.25 gs. lauryl dimethyl amine is added. After one more hour of reaction time, 0.05 g. hydroquinone is added and a nitrogen sparge is started. Then 1.49 g. methacrylic acid is added and the temperature of the reaction mixture is maintained at $110^{\circ} \pm 1^{\circ}\text{C}$. until the drop in acid value indicates that 25% of the glycidyl rings have been esterified (ca. 6 hrs.). The batch is cooled to 50°C . and added slowly to 2700 mls. of methyl alcohol with continuous vigorous agitation. The precipitated polymer is allowed to settle for 24 hours and is recovered by decantation. The polymer is airdried at room temperature for 48 hours and then for 4 hours at 50°C . This polymer is then dissolved in 300 gs. of Isopar G giving a deep clear orange solution to be used in latex production.

EXAMPLE IX

In a 500 ml. resin reactor equipped with a stirrer, a thermometer, a reflux condenser open to the atmosphere, a nitrogen bubbler and a dropping funnel is placed 197.8 gs. Isopar K and warmed to $110^{\circ} \pm 1^{\circ}\text{C}$. A mixture of 86.0 gs. lauryl methacrylate, 9.9 gs. N-1, 1, 3, 3-tetramethyl butyl methacrylamide, 2.97 gs. glycidyl methacrylate and 0.74 gs. benzoyl peroxide is placed in the dropping funnel and added to the hot solvent at a constant rate over a 3 hr. period, the temperature being maintained at $110^{\circ} \pm 1^{\circ}\text{C}$. The polymerization is allowed to continue for 6 more hours after the last of the monomer mixture has been added (a sample of the mixture analyzed at this time reveals a 96.4 percent polymerization). Then 0.12 gs. lauryl dimethyl amine is added to the mixture and it is heated for another hour at which time 0.05 g. hydroquinone is added and a nitrogen sparge begins. Next 1.49 gs. methacrylic acid is added and the temperature of the mixture maintained at $110^{\circ} \pm 1^{\circ}\text{C}$. until a check of the acid content indicates that 25 percent of the glycidyl rings have been esterified (ca. 9 hrs.). The product is a somewhat viscous, straw-colored liquid.

LATICES

The following are examples of latices prepared in accordance with the present invention employing those of the foregoing precursors which yield better results.

EXAMPLE X

In a 500 ml. resin reactor open to the atmosphere, and equipped with a stirrer, a thermometer and a reflux condenser, is placed 360 g. Isopar K, 185 gs. vinyl acetate, 30 gs. of the precursor prepared according to EXAMPLE IV, 15 gs. methyl hydrogen maleate and 4 gs. AZBN. The temperature of the reaction mixture is raised to $85^{\circ} \pm 2^{\circ}\text{C}$. and held there for 4 hours. An additional 2 gs. of AZBN is then added to the mixture and the polymerization is carried out for another 4 hours at $85^{\circ} \pm 2^{\circ}\text{C}$. A thin blue white latex is obtained with a particle size of 0.04 to 0.2 microns.

EXAMPLE XI

A mixture of 27.5 gs. of the precursor solution prepared according to EXAMPLE V, 30 g. methyl methacrylate, 0.5 g. methacrylic acid and 0.4 g. AZBN is charged along with 134 g. petroleum ether (b.p. 60° – 90°C .) and 29.5 g. Isopar G into a 500 ml. resin reactor open to the atmosphere and is gently refluxed for 20 minutes. Then 1.4 g. of a 10 percent solution by weight of n-octyl mercaptan in Isopar K is added to the reactor. A mixture of 166. g. methyl methacrylate, 3.4 g. methacrylic acid 3.0 g. of the 10 percent solution of n-octyl mercaptan in Isopar K, and 0.4 g. AZBN is dripped at a constant rate over a period of 2½ hours. Gentle reflux is continued for another one-half hour and the batch is then cooled to room temperature. The resulting product is a smooth, white, slightly viscous latex with a particle size of 0.4–1.0 microns.

EXAMPLE XII

In a 2 liter 3-neck round-bottom flask open to the atmosphere and equipped with a stirrer, a thermometer, and a reflux condenser is placed 848.5 g. Isopar K, 70.7 g. of the precursor solution prepared according to EXAMPLE VIII, 471.4 g. vinyl acetate and 9.4 g. AZBN. The reaction mixture is heated with constant agitation to 86°C . and the temperature is maintained for 4 hours. The resulting product is a light lemon yellow latex with a particle size less than 0.2 micron and a solids content of 31.7 percent.

EXAMPLE XIII

A mixture of 18 g. of the precursor solution prepared according to EXAMPLE V, 110 g. hydroxypropyl methacrylate, 3 g. AZBN and 200 g. Isopar K is placed into a 500 ml. resin reactor open to the atmosphere and heated with constant agitation. The exotherm begins at 78° – 80°C . and the temperature rises to a maximum of 120°C . and then drops back to 80°C . Polymerization is complete in 30 minutes. A slight amount of over-size large particle material is removed by pouring the mixture through a 200 mesh nylon screen. A white latex of 0.5 micron particle size is obtained.

EXAMPLE XIV

A solution of 15 g. of Bakelite Union Carbide poly (vinyl ethyl ether) (Vinylite EDBM, a poly(vinyl ethyl ether) with a reduced viscosity of 4.0 ± 0.5 as determined by using 0.1 g. polymer in 100 mls. benzene at 20°C ., Sp.Gr. 0.968 at 20°C .) in 285 g. of Isopar G is

25

made in a 500 ml. resin reactor open to the atmosphere through a reflux condenser by shaving the resin into small particles and agitating it in the solvent at 90°C. for 20 hours. The solution is cooled to room temperature and 185 g. vinyl acetate and 2.0 g. benzoyl peroxide (99%) is added. The batch is heated until reflux occurs (ca. 95°C.) and the temperature is maintained for 4 hours. After 45 minutes of heating at said temperature, the solution becomes turbid. After 1 hr. 15 mins. of heating at said temperature the batch becomes so viscous that although the stirrer continues to run, no agitation is visible and the product appears to be a thick white cream. After 2 hours of heating at said temperature the batch begins to thin and at the end of 3 hours of such continued heating it thins to the consistency of heavy cream where it remains. At the end of the 4 hours, the dropwise addition of a solution of 1.5 g. lauroyl peroxide in 30 gs. Isopar G is begun and completed over a 3 hour period while the temperature of the system is maintained at $95^{\circ} \pm 2^{\circ}\text{C}$. The mixture is held at this temperature for 3 more hours after the last of the lauroyl peroxide solution has been added. The result is a white latex of 0.7–1.5 micron particle size.

EXAMPLE XV

A mixture of 180 g. Isopar K, 100 gs. vinyl acetate, 15 gs. precursor solution prepared according to EXAMPLE VI, and 2 gs. AZBN is placed in a 500 ml. reaction flask equipped with a thermometer, a stirrer, a reflux condenser and an internal cooling coil. The reacting mixture is heated to and maintained at $86^{\circ} \pm 2^{\circ}\text{C}$. for 4 hours with continuous agitation. The flask is open to the atmosphere through the cooled reflux condenser. Occasionally it is necessary to cool the reacting mixture by running water through the cooling coil during the early stages of the reaction. The resulting product is a thin white to bluewhite latex whose particles are too small to be viewed in an optical microscope. The latex contains 33 percent solids.

EXAMPLE XVI

In a 5 liter jacketed glass reactor equipped with a thermometer, a stirrer and a reflux condenser (the apparatus of EXAMPLE VI) is placed 2160 gs. Isopar K, 180 gs. precursor prepared according to EXAMPLE V, 1140 gs. vinyl acetate, 60 gs. N-vinyl-2-pyrrolidone and 24 gs. AZBN. The reaction mixture is heated to and maintained at $86 \pm 2^{\circ}\text{C}$. for 4 hours. The resulting product is a thin white to blue-white latex whose particles are too small to be viewed in an optical microscope.

EXAMPLE XVII

In a 500 ml. resin reactor open to the atmosphere and equipped with a stirrer, a thermometer and a reflux condenser is placed 360 g. Isopar K, 190 gs. vinyl acetate, 30 gs. of the precursor prepared according to EXAMPLE V, 10 gs. crotonic acid and 4 gs. AZBN. The temperature of the reaction mixture is raised to $85^{\circ} \pm 2^{\circ}\text{C}$. and held there for 4 hours. An additional 2 gs. of AZBN is then added to the mixture and the polymerization is carried out for another 4 hours at $85^{\circ} \pm 2^{\circ}\text{C}$. A thin white latex is obtained.

EXAMPLE XVIII

In a 500 ml. resin reactor open to the atmosphere and equipped with a stirrer, a thermometer, a thermoregulator, a reflux condenser and an internal cooling coil is

26

placed 40 gs. Lube Oil Additive 564 (Dupont, a 40 percent by weight solution of a 90:10 lauryl methacrylate: diethylaminoethyl methacrylate copolymer in kerosene), 284 gs. Isopar K and 2.2 gs. benzoyl peroxide (99%). With continuous agitation, the batch is heated to 80°C. and maintained at that temperature for 2 hours. At this time a mixture of 10 gs. crotonic acid and 190 gs. vinyl acetate is added all at once to the reacted precursor which has become a dark amber. When the temperature of the reaction mixture has returned to 80°C., AZBN is added to the mixture in 0.2 g. increments at 10 min. intervals until a total of 4.6 gs. has been added (3 hrs. 40 min.). The reaction mixture is maintained at $80^{\circ} \pm 2^{\circ}\text{C}$. for 2 hours after the addition of the AZBN is complete. A white latex is obtained of 35.7% solids with a particle size <0.3 micron.

EXAMPLE XIX

An example of a dyeing procedure for a latex in which it is believed that the dye does not react with the latex (although it is possible that it may be associated therewith by hydrogen bonding) is a mixture of 10% by weight Sudan Orange RA (Solvent Yellow 14, C.I. No. 12055) in Isopar K the same being ball milled for 4 hours. Twenty gs. of this dispersion is added to 100 gs. of the latex prepared according to EXAMPLE XVII and the mixture is heated at 130°–135°F. for 8 hours with constant mechanical agitation. The mixture is filtered through a 200 mesh nylon cloth and allowed to cool to room temperature. A golden orange-colored latex is obtained.

TONERS

The following are typical examples of working toners prepared in accordance with the present invention and employing some of the foregoing precursors.

EXAMPLE XX

One hundred gs. of the latex produced in EXAMPLE XVIII is placed in a 500 ml. 3-neck round-bottom open top flask equipped with a stirrer, a reflux condenser and a thermometer, and 2 gs. of Victoria Blue Base BA (C.I. No. 44045B) is added to it. The temperature is raised to $90^{\circ} \pm 5^{\circ}\text{C}$. and held there for 2 hours. The blue latex which results is cooled and filtered through a 200 mesh nylon cloth to remove residual dye. Four gs. of this dyed latex is diluted with 2000 mls. Isopar K and 8 drops of a 1 percent solution of aluminum 3, 5-diisopropylsalicylate in Isopar K is added. This latex is a complex molecule including in addition to the solvated and non-solvated moieties (in the liquid solvent system) a chromophore moiety. The charge director is a separate compound. When used as a toner bath in a Dennison Standard Book Copier, beautiful blue prints are obtained which are background-free and smear-proof.

EXAMPLE XXI

To the batch of latex as prepared in EXAMPLE XVII is added 13.65 gs. Victoria Blue Base BA and the temperature of the mixture is maintained at $85^{\circ} \pm 2^{\circ}\text{C}$. for 3 hours. The dark blue latex is filtered through a 200 mesh nylon cloth and cooled to room temperature. This toner likewise represents an example of a chromophoric moiety which is part of a complex amphipathic molecule. Four gs. of this latex is added to 2000 mls. Isopar G along with 20 drops of a 1 percent solution of the aluminum salt of 3,5-di-t-butyl gamma resorcylic

acid in Isopar G. This mixture, when used as a bath in a Dennison Standard Book Copier, gives intense, bright blue images which are background-free and smear-proof.

EXAMPLE XXII

To the batch of latex as prepared in EXAMPLE X is added 6.8 gs. Auramine O and 6.8 gs. Rhodamine and the temperature of the mixture is maintained at $85^{\circ} \pm 2^{\circ}\text{C}$. for 3 hours. The now bright yellow-orange latex is filtered through a 200 mesh nylon cloth and cooled to room temperature. This toner likewise represents an example of a chromophoric moiety which is part of a complex amphipathic molecule. Ten gs. of this latex is added to 2000 mls. Isopar G along with 20 drops of a 1 percent solution of the aluminum salt of 3,5-di-t-butyl gamma resorcylic acid in Isopar G. This mixture, when used as a bath in a Scott 3 D Copier, gives extremely bright orange images which are background-free, smear-proof, and exhibit a bright orange fluorescence when exposed to ultraviolet radiation.

EXAMPLE XXIII

To the batch of latex as prepared in EXAMPLE X is added 13.65 gs. Victoria Green and the temperature of the mixture is maintained at $25 \pm 2^{\circ}\text{C}$. for 48 hours. The now dark bluish green latex is filtered through a 200 mesh nylon cloth and cooled to room temperature. This toner likewise represents an example of a chromophoric moiety which is part of a complex amphipathic molecule. Four gs. of this latex is added to 2000 mls. Isopar G along with 20 drops of a 1 percent solution of the aluminum salt of 3,5-di-t-butyl gamma resorcylic acid in Isopar G. This mixture, when used as a bath in a Dennison Standard Book Copier, gives intense, bright bluish green images which are background-free and smear-proof.

EXAMPLE XXIV

Three gs. of the latex prepared according to EXAMPLE XV are ground together with 0.25 gs. of Raven 11 in a mortar and pestle. The resulting paste is thinned with a little Isopar K and finally diluted to a volume of 2000 mls. with Isopar K. To this suspension is added 30 drops of a 1 percent solution of the aluminum salt of 3,5-di-t-butyl gamma resorcylic acid. When this suspension is used as a toner bath in a Dennison Standard Book Copier, good prints completely free from smearing are obtained.

EXAMPLE XXV

To the batch of latex as prepared in EXAMPLE XVII is added 13.65 gs. Crystal Violet (C.I. No. 42555B) and the temperature of the reaction mixture is maintained at $85^{\circ} \pm 2^{\circ}\text{C}$. for 3 hours. This toner likewise represents an example of a chromophoric moiety which is part of the complex amphipathic molecule. The colored latex is filtered through a 200 mesh nylon cloth and cooled to room temperature. Three gs. of this latex is added to 2000 mls. Isopar K along with 0.05 gs. aluminum dresinate. This bath, when used in an A-M Sunbeam 500 Copier, gives very good violet prints with no background.

EXAMPLE XXVI

To the batch of latex as prepared in EXAMPLE XVII is added 13.65 gs. Magenta (C.I. No. 42510B) and the temperature of the reaction mixture is maintained at

$85^{\circ} \pm 2^{\circ}\text{C}$. for 3 hours. The colored latex is filtered through a 200 mesh nylon cloth and cooled to room temperature. This toner likewise represents an example of a chromophoric moiety which is part of the complex amphipathic molecule. Three gs. of this latex is added to 2000 mls. Isopar G along with 0.05 gs. aluminum dresinate and 20 gs. of a 10 percent solution of Aerosol OT in Isopar K. When used as a toner bath in a Dennison Standard Book Copier, magenta prints, virtually smear-proof and background-free, are obtained.

EXAMPLE XXVII

This is an example of a reversal developer. To the batch of latex as prepared in EXAMPLE XVII is added 13.65 of Victoria Blue (C.I. No. 44045B) and the temperature of the reaction mixture is maintained at $85^{\circ} \pm 2^{\circ}\text{C}$. for 3 hours. The colored latex is filtered through a 200 mesh nylon cloth and cooled to room temperature. This toner likewise represents an example of a chromophoric moiety which is part of the complex molecule. Six gs. of this latex is added to 2000 mls. Isopar K along with 0.6 gs. OLOA 1200. This bath, when used in an A-M Sunbeam Copier, gives good blue reversal prints.

EXAMPLE XXVIII

This is an example of a reversal developer. To the batch of latex as prepared in EXAMPLE X is added 6.8 gs. Auramine O and 6.8 gs. Rhodamine and the temperature of the mixture is maintained at $85^{\circ} \pm 2^{\circ}\text{C}$. for 3 hours. The now bright yellow-orange latex is filtered through a 200 mesh nylon cloth and cooled to room temperature. This toner likewise represents an example of a chromophoric moiety which is part of the complex molecule. 8.0 gs. of this latex are added to 2500 mls. of Isopar G along with 100 μ liters of a 34.8 percent by weight solution of the aluminum salt of a 50—50 by weight mixture of the mono- and di-2 ethylhexyl esters of phosphoric acid in Isopar H and 10 mls. of a 10% by weight solution of Alkanol DOA in Isopar H. This mixture, when used as a bath in a Scott 30 Copier, gives extremely bright orange reversal prints.

EXAMPLE XXIX

Four gs. of the latex produced according to the EXAMPLE XIX is added to 2000 mls. Isopar K along with 20 drops of a 1 percent solution of aluminum diisopropyl salicylate in Isopar G. This mixture, when used as a bath in a Dennison Standard Book Copier, gives yellowish-orange images which are background-free and smear-proof.

The foregoing toner examples have each time mentioned but a single color agent. Optionally, plural coloring agents may be used and it is usually preferred to employ two or more color agents, the conjoint action of which is to produce a deep color such, for example, as a brown-black, blue-black or purple-black.

The present invention can be carried out in still another fashion, although it still involves, of course, the use of a multifunctional complex molecule having a polymeric moiety solvated by and a polymeric moiety unsolvated by the liquid solvent system; this is to form the amphipathic polymer molecule in a solvent in which such molecule is completely solvated and then by adding another solvent which is a nonsolvent for a moiety of the polymer but is miscible with the first solvent, and desolvating this moiety of the amphipathic polymer molecule while said desolvated moiety remains bonded to the solvated moiety of the polymer,

i.e., remains as a part of the polymer. If desired, all or a part of the first solvent can then be withdrawn. This is an extremely easy general way for obtaining a block amphipathic polymer as the dispersed phase in accordance with the present invention. As an example of the foregoing a block polymer of polyisoprene-polystyrene-polyisoprene is formed by anionic polymerization.

EXAMPLE XXX

9.2 gs. of styrene are added to 60 cc. of tetrahydrofuran containing 3.3×10^{-4} mole of sodium naphthalene (a catalyst) at -80°C . in a three-neck round bottom flask equipped with a mechanical stirrer, a thermometer and a nitrogen inlet in a dry ice bath. The reaction is completed in 15 minutes, resulting in the formation of a "living" polystyrene polymer. Upon completion of polymerization 6.3 gs. of isoprene is added (still at -80°C .) and the isoprene polymerizes on the living ends of the polystyrene to form a block polymer. The now living ends of this block polymer, which block polymer is solvated by the tetrahydrofuran, are then grafted on to a suitable backbone polymer as by reacting at room temperature with 3 gs. of the precursor solution of EXAMPLE VIII to form the amphipathic polymer. Said backbone (precursor) polymer likewise is solvated by the tetrahydrofuran and such polymer is made the solvated phase of a nonsolvent for the block polymer of the system. Thereby the block polymer moiety is desolvated. The non-solvent employed is OMS which is added at room temperature to the solvated poly (styrene/isoprene)/poly (lauryl methacrylate - glycidyl methacrylate - methacrylic acid - p-phenolazoacrylanilide) amphipathic polymer to form a latex. To transform this colored (golden-yellow) latex into a working toner there is added to 15 gs. of the latex 2000 ml. of OMS and 30 drops of a 1 percent solution of the aluminum salt of 3,5-di-t-butyl gamma resorcylic acid. When this toner is employed as a bath in a Dennison Standard Book Copier good prints are obtained.

There have been mentioned above various characteristics of the toner of the present invention, and specifically the fact that it provides a mono-dispersed particle size and makes use of an amphipathic molecule which has the ability to be either bifunctional or tri-functional. However, there are further advantages to the unique toner which, like the ones just mentioned, are of very substantial commercial importance. These include the ability of the new toner to provide a very quick fixing of a freshly developed image, as well as the ability to function in widely diverse types of equipment wherein liquid electrostatic toners are employed.

Referring to the fast-acting fixation characteristic of the new toner, the same is specially useful in high speed development. The present toner can, of course, be employed in all conventional electrostatographic copy machines, both office copy machines which are found, e.g., in small offices, and somewhat higher speed copy machines such as machines which produce 660, 2400 and 3600 printed sheets per hour, which machines, as soon will be seen, are relatively slow. There are other uses where a liquid electrostatic toner could be widely employed if only the fixing were sufficiently rapid. One such use is for computer read-outs. Computers as a class have an ability to generate information at a tremendous rate. The current generation of computers has the ability to generate as many as a billion characters a second. This is far beyond the capability of elec-

trostatic development due, principally, to the comparatively slow speed at which the initial fixing takes place. This initial fixing occurs between the time that the electrostatic substrate with the freshly developed image on it leaves the developer and the time that the image is to be physically manipulated by equipment in a manner such that the freshly developed image is touched by a piece of equipment or a reverse side of another substrate or a part of the same substrate. By this it is meant that the substrate with the freshly electrostatically developed image, after passing through a dryer which handles the substrate by its edges, has to be compacted. The compaction usually will be by rolling up the substrate into the form of a convoluted cylinder or manifolding it, e.g., fan-folding it. If the freshly developed image at this time, which, e.g., is 20 seconds after it has left the developing bath, is not fully fixed, it will tend to smear or off-set, both of which make the process economically undesirable. The toner of the present invention, however, makes an initial fix of the freshly developed image so quickly that this problem has been overcome. In other words, the toner of the present invention will electrostatically develop an image which, within as little as 20 seconds after formation and even without the necessity of applying heat, will be set to the point where the substrate bearing the image can be handled by machine parts or pressed against a reverse face of another substrate or another part of the substrate without causing smearing. Accordingly, the new toner is particularly useful for rapid development despite the fact that it is also very advantageous to use in ordinary electrostatographic development at lesser output rates.

It also should be observed that the new toner can be employed in such widely diverse types of equipment as the enlarged reproduction of microfilms, either at normal speeds or at high speeds. It further can be used in the reproduction section of facsimile receiving equipment and it forms an excellent electrostatic developer for instrument recording, whether the instrument employs as the moving element an electron beam or an actinic beam, which may be caused to leave a trace on a statically charged substrate by a mirror movable about plural axes.

An additional advantage of the new toner is that it can be used with equal facility to develop both actinically sensitive and actinically non-sensitive electrostatic types of substrates, so that the same principle can be employed in making the toner regardless of which end use is to be employed. Still another type of equipment with which the new toner is fully compatible is electrophotographic cathode ray apparatuses, such, e.g., as the Stromberg Datagraphix. In this type of equipment an electrostatic latent image is formed with the use of a cathode ray tube and is printed off, i.e., transferred, to a uniformly charged zinc oxide paper, the process essentially being an electrophotographic one. Still another type of apparatus that can be employed with the new toner is the A.B. Dick Videograph in which the latent image is formed with the aid of a cathode ray pin tube. Nor should one overlook the ability of the toner to be used with the Varian Statos recorder. Furthermore, the novel toner of the present invention can be utilized by direct application in the manufacture of printed circuit boards.

In all of the foregoing uses mentioned just above the toner is utilized to form a visible deposit or representation by preferential attraction to a differentially elec-

trostatically charged substrate. However, the toner is not limited to this kind of process and can be used in other processes where, in general, the liquid toner is characterized by the presence of a liquid solvent system carrying colored particles or coloring in general. The toner of the present invention, thus, can be and has been successfully employed in jet ink beam printing wherein the toner is shaped into a moving fine stream which is projected from a portion of the apparatus on to a graphic reception type of substrate which need not be electrostatically charged. The jetted beam of ink, preferably broken up into droplets, has its flight path controlled by passage between pairs of electrostatic deflecting plates, these plates altering the physical orientation of the parts of the beam passing between them by varying the electrostatic charge thereon as a function of certain intelligence which is fed into the plates. Such method can be practiced only because the liquid solvent system is highly non-conductive and, therefore, capable of being charged so as to react properly with fluctuating electrostatic fields through which it passes. The toner of the present invention is particularly efficient in equipment of this character because of its low viscosity which permits the jet to be formed into a very fine beam and because of its high surface tension which facilitates the subdivision of the beam into droplets so that the same can be moved with greater celerity by electrostatic means.

Not to be overlooked in any of the foregoing is the fact that, in addition to the quick initial fixing which avoids ready smearing while the image is still fresh, the present toner has the decided advantage that a fully dried image will not smear even when deliberate efforts are made to distort the image as by rubbing a finger across a developed image. It is believed that the initial ability to resist smearing of a freshly developed image and the subsequent ability to resist smearing of an image in handling by people is largely due to the fact that, with an amphipathic molecule of the character which predominates in the toner of the instant invention, the liquid solvent system more readily disassociates from the molecule so as to escape into the ambient atmosphere and leave a quickly initially substantially, and subsequently fully, dried developed visible area. Also the solvent is able to escape more readily from a deposited film principally constituted of such amphipathic molecules.

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

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

Having thus described the invention, there is claimed as new and desired to be secured by Letters Patent:

1. A liquid electrostatographic toner essentially comprising a liquid solvent system, amphipathic polymeric molecules of the graft type each having a polymeric backbone part and a polymeric graft part on said backbone part, each of said molecules being composed of two moieties of which at least one is thermoplastic, said first moiety, which is one of said parts, being solvated by said system, a portion of said first moiety being a dispersant and a fixative to bond the molecules to a substrate, and a second moiety, which is the other of said

parts, being insoluble in said system, said second moiety having a particle size between 25μ and 25μ , a portion of said second moiety being a fixative to bond the molecules to a substrate, so that there is provided a continuous phase constituting the solvent system with the first moieties of the molecules dissolved therein and a dispersed phase constituting the non-solvated moieties of the molecules whereby said molecules act as a mono-dispersed particle phase, a fixative and a dispersant, and a charge director.

2. A liquid toner as set forth in claim 1 which further includes a color agent.

3. A liquid toner as set forth in claim 1 wherein the charge director imparts a resistivity to the toner of from 10^{14} to no less than 10^9 ohms cms.

4. A liquid toner as set forth in claim 1 wherein the charge director imparts a resistivity to the toner of from 10^{13} to 10^{10} ohms cms.

5. A liquid toner as set forth in claim 1 wherein the charge director imparts a resistivity to the toner of from 2×10^{12} to 10^{11} ohms cms.

6. A liquid toner as set forth in claim 2 wherein a color agent is a moiety of the amphipathic molecule.

7. A liquid toner as set forth in claim 2 wherein the color agent is a compound other than the amphipathic molecule.

8. A liquid toner as set forth in claim 1 wherein the amphipathic molecule includes a solvated moiety selected from the class consisting of crepe rubber; refined linseed oil; degraded rubber; alkyd resins, polyisobutylene; polybutadiene; polyisoprene; polyisobornyl methacrylate; homopolymeric vinyl esters of long chain fatty acids; homopolymeric vinyl alkyl ethers; homopolymers of the C_4 - C_{22} alkyl esters of acrylic and methacrylic acid in a molecular weight range of about 10^3 to about 10^6 ; copolymers of the aforesaid C_4 - C_{22} alkyl esters with one another; copolymers of the aforesaid C_4 - C_{22} alkyl esters with one another and with methyl, ethyl, isopropyl and propyl esters of acrylic and methacrylic acids; copolymers of the C_4 - C_{22} alkyl esters of acrylic and methacrylic acids with monomers containing acrylic acid, methacrylic acid, crotonic acid, maleic acid, atropic acid, fumaric acid, itaconic acid, citraconic acid, acrylic anhydride, methacrylic anhydride, maleic anhydride, acryloyl chloride, methacryloyl chloride, acrylonitrile, methacrylonitrile, N-vinyl pyrrolidone, acrylamide and derivatives thereof, methacrylamide and derivatives thereof, hydroxyethyl methacrylate, hydroxyethyl acrylate, hydroxypropyl methacrylate, hydroxypropyl acrylate, dimethylaminomethyl methacrylate, dimethylaminomethyl acrylate, dimethylaminoethyl methacrylate, dimethylaminoethyl acrylate, diethylaminomethyl methacrylate, diethylaminomethyl acrylate, diethylaminoethyl methacrylate, diethylaminoethyl acrylate, t-butylaminoethyl methacrylate, t-butylaminoethyl acrylate, cyclohexyl acrylate, allyl alcohol and derivatives thereof, cinnamic acid and derivatives thereof, styrene and derivatives thereof, butadiene, methallyl alcohol and derivatives thereof, propargyl alcohol and derivatives thereof, indene and derivatives thereof, norbornene and derivatives thereof, vinyl ethers, vinyl esters, vinyl derivatives other than vinyl ethers and vinyl esters, glycidyl methacrylate, glycidyl acrylate, mono- and dimethyl maleate, mono- and dimethyl fumarate, mono- and diethyl maleate and mono- and diethyl fumarate; condensation polymers; copolymers of butadiene, isoprene and isobutylene with C_4 - C_{22} alkyl esters of acrylic and meth-

acrylic acids; polycarbonates; polyamides; polyurethanes and epoxies, and the nonsolvated moiety comprises homopolymers and copolymers formed from monomers selected from the class consisting of vinyl acetate, vinyl chloride, methyl acrylate, methyl methacrylate, ethyl acrylate, ethyl methacrylate, propyl acrylate, propyl methacrylate, isopropyl acrylate, isopropyl methacrylate, hydroxy ethyl acrylate, hydroxy ethyl methacrylate, hydroxy propyl acrylate, hydroxy propyl methacrylate, acrylonitrile, methacrylonitrile, acrylamide, methacrylamide, acrylic acid, acrylic anhydride, methacrylic acid, methacrylic anhydride, mono methyl maleate, mono methyl fumarate, mono ethyl maleate, mono ethyl fumarate, styrene, vinyl toluene, maleic acid, maleic anhydride crotonic acid, crotonic anhydride, fumaric acid, atropic acid, allylamine, vinyl amine, allyl alcohol, vinyl pyridines and derivatives thereof, glycidyl acrylate, glycidyl methacrylate, dialkylaminoalkyl methacrylate, dialkylaminoalkyl acrylate, methacrylyl acetone, N-hydroxymethyl methacrylamides, alkoxymethyl methacrylamides, acryloyl chloride, methacryloyl chloride, vinyl isocyanate, cyanomethylacrylate, vinyl β -chloroethylsulphone, vinyl sulphonic acid and vinyl phosphoric acid.

9. A liquid toner as set forth in claim 1 wherein the charge director is selected from the class consisting of di-2-ethylhexyl sodium sulfosuccinate; di-tridecyl sodium sulfosuccinate; aluminum, chromium, zinc and calcium salts of 3, 5-dialkylsalicylic acid, wherein the alkyl group is propyl, isopropyl, butyl, isobutyl, tertiary butyl, amyl, isoamyl and other alkyl groups up to C-18; aluminum, chromium, zinc and calcium salts of dialkyl gamma-resorcylic acid, wherein the alkyl is as above; isopropylamine salt of dodecylbenzene sulfonic acid; aluminum, vanadium and tin dresinates; aluminum stearate; cobalt, iron and manganese octoates; a partially imidized polyamine with lubricating-oil-soluble polyisobutylene chains and free secondary amines, gravity at 60°F API 22.9, specific 0.92, flash point by the Cleveland open cup method, 425°F, viscosity at 210°F, 400 SSU, color (ASTM D-1500) L55D, nitrogen, percentage by weight 2.0, and alkalinity value, (SM-205-15) 43; soya bean lecithin, an aluminum salt of 50/50 by weight mixture of the mono- and di-2 ethylhexyl esters of phosphoric acid, and a terpolymer consisting of 50 percent by weight octadecenyl, methacrylate, 40 percent by weight styrene, and 10 percent by weight diethylaminoethyl methacrylate.

10. A liquid toner as set forth in claim 1 wherein the amphipathic molecule includes a backbone chain of comonomers and attached chains having attached sites of a precursor monomer derived from monomers selected from the affiliated monomer groups set forth below:

Comonomer of backbone chain	Attached site precursor monomer (one or more non-mutually reactive radicals to be selected from each group)
Glycidyl methacrylate or acrylate	- Acrylic acid - Methacrylic acid - Maleic acid - Fumaric acid - Atropic acid - Allylamine - Vinyl amine - Hydroxylethyl methacrylate and acrylate - Hydroxypropyl methacrylate and acrylate
Acryloyl or methacryloyl chloride	- Acrylamide - Methacrylamide

- Continued

Comonomer of backbone chain	Attached site precursor monomer (one or more non-mutually reactive radicals to be selected from each group)
5 Acryloyl or methacryloyl chloride	- Allyl alcohol - Allylamine - Vinyl amine
10 Acrylic acid	Vinyl pyridines
Methacrylic acid	Glycidyl methacrylate
Maleic acid	Vinylamine
Crotonic acid	Allylamine
Alkyl hydrogen maleates	Dialkylaminoalkyl methacryl- ates and acrylates
Alkyl hydrogen fumarates	Allylamine
Vinyl isocyanate	Vinylamine
15 Cyanomethylacrylate	Methacrylyl acetone
Vinyl β -chloroethyl- sulphone	Vinylamine
20 Methacrylic anhydride	Allylamine
Acrylic anhydride	Vinylamine
Maleic anhydride	Allyl alcohol
Vinyl sulphonc acid	Hydroxyalkyl methacrylates
Vinyl phosphoric acid	Glycidyl methacrylate
	Vinylamine
	Allylamine
	Hydroxyalkyl methacrylates
	Allyl alcohol
	N-hydroxymethyl methacryl- amides
	Alkoxymethyl methacrylamides

11. A liquid toner as set forth in claim 1 wherein the solvent system is a liquid petroleum fraction.

12. A liquid toner as set forth in claim 11 wherein the liquid petroleum fraction has an electrical resistivity of at least 10^9 ohm cm., a dielectric constant of less than three and one-half, a TCC flash point of 100°F. to 152°F. and a viscosity of 0.5 to 2.5 centipoises at room temperature.

13. A liquid toner as set forth in claim 2 wherein the chromophore is selected from the class consisting of powdered metals, powdered metal oxides, powdered metal salts, acetamine black CBS, nigrosine base No. 424, Hansa Yellow G, spirit nigrosine SSB, Rubanox Red CP-1495 and carbon black.

14. A liquid toner as set forth in claim 1 wherein the solvated moiety is poly (lauryl methacrylate - glycidyl methacrylate- methacrylic acid).

15. A liquid toner as set forth in claim 14 wherein the non-solvated moiety is poly (vinyl acetate).

16. A liquid toner as set forth in claim 14 wherein the non-solvated moiety is poly (vinyl acetate/N-vinyl-2-pyrrolidone).

17. A liquid toner as set forth in claim 14 wherein the non-solvated moiety is poly (vinyl acetate/crotonic acid).

18. A liquid toner as set forth in claim 14 wherein the non-solvated moiety is poly (vinyl acetate/methyl hydrogen maleate).

19. A liquid toner as set forth in claim 1 wherein the solvated moiety is poly (isodecyl methacrylate-glycidyl methacrylate - methacrylic acid).

20. A liquid toner as set forth in claim 19 wherein the non-solvated moiety is poly (vinyl acetate).

21. A liquid toner as set forth in claim 1 wherein the solvated moiety is poly (stearyl methacrylate - glycidyl methacrylate - methacrylic acid).

22. A liquid toner as set forth in claim 1 wherein the solvated moiety is poly (lauryl methacrylate - glycidyl methacrylate - methacrylic acid - chromophore).

23. A liquid toner as set forth in claim 1 wherein the solvated moiety is poly (lauryl methacrylate - N-

35

1,1,3,3-tetramethyl butyl methacrylamide - glycidyl methacrylate - methacrylic acid).

24. A liquid toner as set forth in claim 1 wherein the non-solvated moiety includes a polymer having recurring units of methyl hydrogen maleate.

25. A liquid toner as set forth in claim 1 wherein the non-solvated moiety is a poly (vinyl acetate/methyl hydrogen maleate).

26. A liquid toner as set forth in claim 6 wherein the chromophore is a dye selected from the class consisting of Pontacyl Brilliant Blue A (Dupont) (C.I. Acid Blue 7); Calcocid Brilliant Blue FFR (American Cyanamid) (C.I. Acid Blue 104); Femazo Brown N (General Aniline) (C.I. Acid Brown 14); Crocein Scarlet N (Du-

36

pont) (C.I. Red 73); Oxanal Yellow I (Ciba) (C.I. Acid Yellow 63); Benzyl Black 4BN (Ciba) (C.I. Black 26A); Magenta (C.I. Solvent Red 41, C.I. No. 42510B); Crystal Violet (C.I. Solvent Violet 9, C.I. No. 42555B); Bismarck Brown (C.I. Solvent Brown 12, C.I. No. 21010B); Victoria Blue BA (C.I. Solvent Blue 4, C.I. No. 44045B); Victoria Blue R (C.I. Solvent Blue 6, C.I. No. 44040R); Victoria Blue 4R (C.I. Solvent Blue 2, C.I. No. 42563B); Copying Black SK (C.I. No. 11975); Janus Green B (C.I. No. 11050); Auramine 0 (C.I. Solvent Yellow 34, C.I. No. 4100B); Victoria Green (C.I. Solvent Green 1, C.I. No. 42000B); and Rhodamine (C.I. Solvent Red 49, C.I. No. 45170B).

* * * * *

20

25

30

35

40

45

50

55

60

65