

[54] **ELECTROGRAPHIC TONER AND DEVELOPER COMPOSITION**
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3,502,582	3/1970	Clemens et al.	252/62.1
3,565,654	2/1971	Story.....	252/62.1
3,647,696	3/1972	Olson.....	252/62.1
R25,136	3/1962	Carlson.....	252/62.1

[73] Assignee: **Eastman Kodak Company**, Rochester, N.Y.

FOREIGN PATENTS OR APPLICATIONS

1,117,224	6/1968	United Kingdom.....	252/62.1
1,174,573	12/1969	United Kingdom.....	252/62.1
1,169,703	11/1969	United Kingdom.....	252/62.1
1,034,849	7/1958	Germany	252/62.1

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[21] Appl. No.: **399,226**

Related U.S. Application Data

[63] Continuation-in-part of Ser. No. 257,524, May 30, 1972, abandoned.

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 [51] **Int. Cl.**..... **G03g 9/00**
 [58] **Field of Search**..... 252/62.1; 117/DIG. 4

[57] **ABSTRACT**

The present invention relates to the use of certain quaternary ammonium salts as useful charge control agents for an electrostatic toner composition.

[56] **References Cited**

UNITED STATES PATENTS

3,320,169 5/1967 East et al. 252/62.1

18 Claims, No Drawings

ELECTROGRAPHIC TONER AND DEVELOPER COMPOSITION

This application is a continuation-in-part of U.S. Ser. No. 257,524 abandoned filed May 30, 1972.

This invention relates to electrography and to a particulate toner composition and a dry electrographic developer composition containing such a toner useful in the development of latent electrostatic charge images.

Electrographic imaging and developing processes, eg. electrophotographic imaging processes and techniques, have been extensively described in both the patent and other literature, for example, U.S. Pat. No. 2,221,776 issued Nov. 19, 1940; No. 2,277,013 issued Mar. 17, 1942; No. 2,297,691 issued Oct. 6, 1942; No. 2,357,809 issued Sept. 12, 1944; No. 2,551,582 issued May 8, 1951; No. 2,825,814 issued Mar. 4, 1958; No. 2,833,648 issued May 6, 1958; No. 3,220,324 issued Nov. 30, 1965; No. 3,220,831 issued Nov. 30, 1965; No. 3,220,833 issued Nov. 30, 1965; and many others. Generally these processes have in common the steps of forming a latent electrostatic charge image on an insulating electrographic element. The electrostatic latent image is then rendered visible by a development step in which the charged surface of the electrographic element is brought into contact with a suitable developer mix. Conventional dry developer mixes include toner or marking particles and may also include a carrier vehicle that can be either a magnetic material such as iron filings, powdered iron or iron oxide, or a triboelectrically chargeable, non-magnetic substance like glass beads or crystals of inorganic salts such as sodium or potassium fluoride. The toner or marking particles typically contain a resinous material suitably colored or darkened, for contrast purposes, with a colorant like dyestuffs or pigments such as carbon black.

One method for applying a suitable dry developer mix to a charged image-bearing electrographic element is by the well-known magnetic brush process. Such a process generally utilizes an apparatus of the type described, for example, in U.S. Pat. No. 3,003,462 issued Oct. 10, 1961 and customarily comprises a non-magnetic rotatably mounted cylinder having fixed magnetic means mounted inside. The cylinder is arranged to rotate so that part of the surface is immersed in or otherwise contacted with a supply of developer mix. The granular mass comprising the developer mix is magnetically attracted to the surface of the cylinder. As the developer mix comes within the influence of the field generated by the magnetic means within the cylinder, particles thereof arrange themselves in bristle-like formations resembling a brush. The brush formations that are formed by the developer mix tend to conform to the lines of magnetic flux, standing erect in the vicinity of the poles and laying substantially flat when said mix is outside the environment of the magnetic poles. Within one revolution the continually rotating cylinder picks up developer mix from a supply source and returns part or all of this material to this supply. This mode of operation assures that fresh mix is always available to the surface of the charged electrographic element at its point of contact with the brush. In a typical rotational cycle, the roller performs the successive steps of developer mix pickup, brush formation, brush contact with the electrographic element, eg. a photoconductive element, brush collapse and finally mix release.

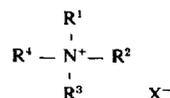
In magnetic brush development, as well as in various other types of electrographic development wherein a dry triboelectric mixture of a particulate carrier vehicle and a toner powder are utilized, e.g., cascade development such as described in U.S. Pat. Nos. 2,638,416 and 2,618,552, it is advantageous to modify the surface properties of the toner powder so that a uniform, stable high net electrical charge may be imparted to the toner powder by the particulate carrier vehicle.

A variety of methods and material for modifying the surface properties of particulate toner particles have been proposed. For example, Olson, U.S. Pat. No. 3,647,696 issued Mar. 7, 1972 describes a uniform polarity resin electrostatic toner containing a mono- or di-functional organic acid nigrosine salt. The nigrosine salt described in U.S. Pat. No. 3,647,696 aids in providing a relatively high uniform net electrical charge to a toner powder containing such a nigrosine salt. However, subsequent testing and development relating to the use of such organic acid nigrosine salts has shown that such materials, when incorporated in a toner composition, contribute to a decrease in the adhesion of the toner particles to a suitable paper receiving sheet. For example, it has been found that when a toner image is transferred from a charge image-bearing electrographic element to a paper receiving sheet and fixed to the receiving sheet, the image formed on the receiving sheets tends to flake off when the sheet is bent or folded.

Other materials which have been employed as modifying agents for dry toner compositions include various long-chain anionic or cationic materials such as various surfactants. Typical of these surfactant materials are the long chain quaternary ammonium surfactants. The use of such materials is described for example in British Pat. No. 1,174,573 published Dec. 17, 1969, at page 2, column 2 through page 3. In addition, Jacknow et al., U.S. Pat. No. 3,577,345 issued May 4, 1971, describes a solid metal salt of a fatty acid admixed with one of various other described solid additives as a useful modifying combination for a dry toner composition.

Other patents which describe various components for use in liquid developers include Beyer, U.S. Pat. No. 3,417,019 issued Dec. 17, 1968, which describes, in part, the use of various metal soaps, for example cobalt naphthenate, for use as a charge control agent in a liquid developer toner composition.

In accordance with the present invention, it has been discovered that certain quaternary ammonium salts incorporated in a dry, particulate toner composition comprising a resin and, if desired, a suitable colorant such as a pigment or dye, provide an effective charge control agent for the toner composition. Typical of the quaternary ammonium salts useful in the present invention are materials having the following formula:



wherein R^1 , R^2 , R^3 and R^4 which may be the same or different represent an aliphatic hydrocarbon group having seven or less, preferably 3 to about 7, carbon atoms, including straight-chain and branched-chain aliphatic hydrocarbon groups, and X^- represents an anionic function.

The quaternary ammonium salt charge control agents, when incorporated in the toner materials of the present invention, have been found surprisingly effective in providing a particulate toner composition which exhibits a relatively high, uniform and stable net toner charge when admixed with a suitable particulate carrier vehicle and which also exhibits a minimal amount of deleterious toner throwoff. The charge control agent used in the present invention has been found substantially more effective than the somewhat related long-chain quaternary ammonium surfactant materials which previously have been incorporated in toner compositions. More specifically, the quaternary ammonium salts of the present invention have been found to exhibit a substantially higher net toner charge and a substantially lower toner throw-off than long-chain quaternary ammonium salt surfactants (or wetting agents as they are sometimes called). (See Example 1 set forth hereinafter.) In addition, the quaternary ammonium charge control agents used in the present invention have been found to have no deleterious effect on the adhesion properties of the resultant toner composition containing these charge control agents to conventional paper receiving sheets.

A further indicia of the uniqueness of the toner compositions of the present invention is the fact that these compositions containing quaternary ammonium salts exhibit substantially better "charge control" properties than toner compositions containing other types of onium salts, e.g., sulfonium, phosphonium, pyridinium, or quinolinium salts. (see Example 1 set forth hereinafter.)

Moreover, it has been found that particulate resinous toner particles containing an effective amount of the above-described quaternary ammonium charge control agents generally result in good to excellent electrographic developed images exhibiting increased and uniform density with little or no background scumming.

The resins useful in the practice of the present invention can be used alone or in combination and include those resins conventionally employed in electrostatic toners. Useful resins generally have a glass transition temperature within the range of from 60° to 120°C. Preferably, toner particles prepared from these resinous materials have relatively high caking temperature, for example, higher than about 55°C., so that the toner powders may be stored for relatively long periods of time at fairly high temperatures without having individual particles agglomerate and clump together. The melting point of useful resins preferably is within the range of from about 65°C. to about 200°C. so that the toner particles can readily be fused to conventional paper receiving sheet to form a permanent image. Especially preferred resins are those having a melting point within the range of from about 65°C to about 120°C. Of course, where other types of receiving elements are used, for example, metal plates such as certain printing plates, resins having a melting point and glass transition temperature higher than the values specified above may be used.

As used herein the terms "melting point" refers to the melting point of a resin as measured by Fisher Johns apparatus, Fisher Scientific Catalog No. 12-144. Glass transition temperature (T_g) as used herein refers to the temperature at which a polymeric material changes from a glassy polymer to a rubbery polymer. This temperature (T_g) can be measured by differential

thermal analysis as disclosed in *Techniques and Methods of Polymer Evaluation*, Vol. 1, Marcel Dekker, Inc., N.Y. 1966.

Among the various resins which may be employed in the toner particles of the present invention are polystyrene containing resins, polycarbonates, rosin modified maleic alkyd resins, polyamides, phenol-formaldehyde resins and various derivatives thereof, polyester condensates, modified alkyd resins and the like, aromatic resins containing alternating methylene and aromatic units such as described in Merrill et al., U.S. Ser. No. 168,389, now Pat. No. 3,809,554 filed Aug. 2, 1971, and the like.

Typical useful toner resins include certain polycarbonates such as those described in U.S. Pat. No. 3,694,359 issued Sept. 26, 1972, and which includes polycarbonate materials containing an alkylidene diarylene moiety in a recurring unit and having from 1 to about 10 carbon atoms in the alkyl moiety. Other useful resins having the above-described physical properties include polymeric esters of acrylic and methacrylic acid such as poly(alkylacrylate) including poly(alkylmethacrylate) wherein the alkyl moiety can contain from 1 to about 10 carbon atoms. Additionally, other polyesters having the aforementioned physical properties are also useful. Among such other useful polyesters are copolyesters prepared from terephthalic acid including substituted terephthalic acid, a bis(hydroxyalkoxy) phenylalkane having from 1 to 4 carbon atoms in the alkoxy radical and from 1 to 10 carbon atoms in the alkane moiety and including such halogen substituted alkanes, and an alkylene glycol having from 1 to 4 carbon atoms in the alkylene moiety.

Other useful resins are various styrene-containing resins. Such polymers typically comprise a polymerized blend of from about 40 to about 100 percent by weight of styrene, from about 0 to about 45 percent by weight of a lower alkyl acrylate or methacrylate having from 1 to about 4 carbon atoms in the alkyl moiety such as methyl, ethyl, isopropyl, butyl, etc. and from about 5 to about 50 percent by weight of another vinyl monomer other than styrene, for example, a higher alkyl acrylate or methacrylate having from about 6 to 20 or more carbon atoms in the alkyl group. A typical styrene-containing resin prepared from a copolymerized blend as described hereinabove are copolymers prepared from a monomeric blend of 40 to 60 percent by weight styrene or styrene homolog, from about 20 to about 50 percent by weight of a lower alkyl acrylate or methacrylate and from about 5 to about 30 percent by weight of a higher alkyl acrylate or methacrylate such as ethylhexyl acrylate. A variety of other useful styrene containing toner materials are disclosed in the following U.S. Pats. No.: 2,917,460 issued Dec. 15, 1959; Re. No. 25,136 issued Mar. 13, 1962; No. 2,788,288 issued Apr. 9, 1957; No. 2,638,416 issued Apr. 12, 1953; No. 2,618,552 issued Nov. 18, 1952 and No. 2,659,670 issued Nov. 17, 1953.

The toner particles of the present invention can be prepared by various methods. One convenient technique for preparing these toners is spray-drying. Spray-drying involves dissolving the polymer and adding the toner colorant and charge control agent to a volatile organic solvent such as dichloromethane. This solution is then sprayed through an atomizing nozzle using a substantially nonreactive gas such as nitrogen as the atomizing agent. During atomization, the volatile solvent

evaporates from the airborne droplets, producing toner particles of the uniformly dyed or pigmented resin. The ultimate particle size is determined by varying the size of the atomizing nozzle and the pressure of the gaseous atomizing agent. Particles of a diameter between about 0.1 micron and about 100 microns may be used, although in general present day office copy devices typically employ particles between about 1.0 and 30 microns. However, larger particles or smaller particles can be used where desired for particular methods of development or particular development conditions. For example, in powder cloud development such as described in U.S. Pat. No. 2,691,345 issued Oct. 12, 1954, extremely small toner particles are used.

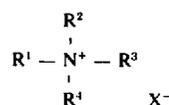
Another convenient method for preparing the toner composition of the present invention is melt-blending. This technique involves melting a powdered form of polymer or resin and mixing it with suitable colorants, such as dyes or pigments, and the charge control agent. The resin can readily be melted on heated compounding rolls which are also useful to stir or otherwise blend the resin and addenda so as to promote the complete intermixing of these various ingredients. After thorough blending, the mixture is cooled and solidified. The resultant solid mass is then broken into small particles and finely ground to form a free-flowing powder of toner particles. These particles typically have an average particle size or average diameter within the range of from about 0.1 to about 100 microns.

As described hereinabove the quaternary ammonium charge control agents of the invention are added to the resinous toner composition in an amount effective to improve the charge properties of the toner composition. The addition of a charge control agent improves the charge uniformity of a particular toner composition, i.e. acts to provide a toner composition in which all or substantially all of the individual discrete toner particles exhibit a triboelectric charge of the same sign (negative or positive) with respect to a given carrier vehicle, increases the net electrical charge exhibited by a specified quantity of toner particles relative to a given carrier vehicle, and reduces the amount of "toner throw-off" of a given toner composition. As used herein, the phrases "net electrical charge exhibited by a toner powder" or "net toner charge" are equivalent and are defined as the total electrical charge exhibited by a specified amount of a particular toner when admixed with a specified amount of a particular carrier vehicle. Although the phenomenon by which such an electrical charge is imparted is not fully understood, it is believed due in large to the triboelectric effect caused by the physical admixture of toner and carrier. As used herein, the term toner throw-off is defined as the amount of toner powder thrown out of a developer mix as it is mechanically agitated, e.g., in a development apparatus. Aside from the extraneous contamination problems inherent with airborne toner dust in the development apparatus, toner throw-off also leads to imaging problems such as unwanted background and scumming of the electrographic image-bearing element.

Generally, it has been found desirable to add from about 0.1 to about 6 parts and preferably 0.3 to about 3.0 parts by weight of the aforementioned quaternary ammonium salts per 100 parts by weight of a resinous binder to obtain the improved toner composition of the present invention. Although larger and smaller

amounts of a charge control agent may be added, it has been found that if amounts much lower than those specified above are utilized, the charge control agent tends to exhibit little or substantially no improvement in the properties of the toner composition. As amounts more than about 6 parts of charge control agent per 100 parts of resinous binder are added, it has been found that the net toner charge exhibited by the resultant toner composition tends to be reduced. Of course, it must be recognized that the optimum amount of charge control agent to be added will depend, in part, on the particular quaternary ammonium charge control agents selected and the particular resinous binder to which it is added. However, the amounts specified hereinabove are typical of the useful range of charge control agent utilized in conventional dry toner materials.

As indicated, the quaternary ammonium charge control agents contemplated for use according to the present invention have the formula:



wherein R¹, R², R³ and R⁴ which may be the same or different represent an aliphatic hydrocarbon group having one to seven carbon atoms and X⁻ is an anionic function. R¹, R², R³ and R⁴ may be a straight chain or branched chain aliphatic hydrocarbon groups including allyl and alkyl moieties, e.g., methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl, isopropyl, etc. Especially good results have been obtained wherein R¹, R², R³ and R⁴ are each an alkyl moiety having 3-7 carbon atoms and wherein each of R¹, R², R³ and R⁴ represents an identical alkyl moiety. As can be observed from the above list, a variety of hydrocarbon substituents may be utilized in the quaternary ammonium salt charge control agents of the present invention. In addition, a variety of conventional anionic moieties may be utilized such as the following: halides such as chloride, bromide, iodide, phosphates; acetates; nitrates; benzoates; methyl sulfate, perchlorate, tetrafluoroborate, benzenesulfonate, and the like. Especially useful anionic moieties are the halides. Typical of the quaternary salts useful in the invention are the following:

Tetrapentylammonium chloride
Tetraheptylammonium chloride
Tetrapentylammonium hexafluorophosphate
Tetraethylammonium benzoate
Tetraethylammonium acetate tetrahydrate
Tetrapentylammonium bromide
Tetrabutylammonium iodide
Tetrabutylammonium nitrate
Triethylmethylammonium iodide

A variety of colorant materials selected from dyes or pigments may be employed in the toner materials of the present invention. Such materials serve to color the toner and/or render it more visible. Of course, suitable toner materials having the appropriate charging characteristics can be prepared without the use of a colorant material where it is desired to have a developed image of low optical opacity. In those instances where it is desired to utilize a colorant, the colorants used, can, in principle, be selected from virtually any

of the compounds mentioned in the *Colour Index* Volumes 1 and 2, Second Edition.

Included among the vast number of useful colorants would be such materials as Hansa Yellow G (C.I. 11680), Nigrosine Spirit soluble (C.I. 50415) Chromogen Black ET00 (C.I. 45170), Solvent Black 3 (C.I. 26150), Fuchsine N (C.I. 42510), C.I. Basic Blue 9 (C.I. 52015), etc. Carbon black also provides a useful colorant. The amount of colorant added may vary over a wide range, for example, from about 1 to about 20 percent of the weight of the thermoplastic resin. Particularly good results are obtained when the amount is from about 2 to about 10 percent. In certain instances, it may be desirable to omit the colorant, in which case the lower limit of concentration would be zero.

The toners of this invention can be mixed with a carrier vehicle to form developing compositions. The carrier vehicles which can be used with the present toners to form new developer compositions can be selected from a variety of materials. Suitable carrier vehicles useful in the invention include various nonmagnetic particles such as glass beads, crystals of inorganic salts such as sodium or potassium chloride, hard resin particles, metal particles, etc. In addition, magnetic carrier particles can be used in accordance with the invention. In fact, the toner compositions of the present invention are especially suited for use with magnetic carrier particles as the problem of toner throw-off is especially bothersome in magnetic brush development processes. Suitable magnetic carrier particles are particles of ferromagnetic materials such as iron, cobalt, nickel, and alloys and mixtures thereof. Other useful magnetic carriers are ferromagnetic particles overcoated with a thin layer of various film-forming resins, for example, the alkali-soluble carboxylated polymers described in Miller, U.S. Pat. No. 3,547,822 issued Dec. 15, 1970; Miller, U.S. Pat. No. 3,632,512 issued Jan. 4, 1972; McCabe, U.S. Ser. No. 236,765, now Pat. No. 3,795,617 filed Mar. 21, 1972, entitled "Electrographic Carrier Vehicle and Developer Composition - Case B"; Kasper et al., U.S. Ser. No. 236,584, now abandoned, filed Mar. 21, 1972, entitled "Electrographic Carrier Vehicle and Developer Composition - Case C"; and Kasper U.S. Ser. No. 236,614, now U.S. Pat. No. 3,795,618 filed Mar. 21, 1972, entitled, "Electrographic Carrier Vehicle and Developer Composition - Case D". Other useful resin coated magnetic carrier particles include carrier particles coated with various fluorocarbons such as polytetrafluoroethylene, polyvinylidene fluoride, and mixtures thereof including copolymers of vinylidene fluoride and tetrafluoroethylene.

A typical developer composition containing the above-described toner and a carrier vehicle generally comprises from about 1 to about 10 percent by weight of particulate toner particles and from about 90 to about 99 percent by weight carrier particles. Typically, the carrier particles are larger than the toner particles. Conventional carrier particles have a particle size on the order of from about 30 to about 1200 microns, preferably 60-300 microns.

The toner and developer compositions of this invention can be used in a variety of ways to develop electrostatic charge patterns or latent images. Such developable charge patterns can be prepared by a number of means and be carried for example, on a light sensitive photoconductive element or a non-light sensitive die-

lectric-surfaced element such as a receiver sheet. One suitable development technique involves cascading the developer composition across the electrostatic charge pattern; while another technique involves applying toner particles from a magnetic brush. This latter technique involves the use of a magnetically attractable carrier vehicle in forming the developer composition. After imagewise deposition of the toner particles, the image can be fixed by heating the toner to cause it to fuse to the substrate carrying the toner. If desired, the unfused image can be transferred to another support such as a blank sheet of copy paper and then fused to form a permanent image.

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

EXAMPLE 1

A poly(4,4'-isopropylidene diphenyl-alt-ethylene carbonate) resin as described in Ser. No. 34,557 filed May 4, 1970 is melted on a rubber compounding mill at a temperature of between 125°-150°C. Cabot Corporation Sterling FT Carbon Black is added to yield 5.7 parts of carbon black per 100 parts of polymer. This carbon black-polycarbonate composition is then used as a control toner. A variety of different materials are then added to individual samples of the control toner as described below and then the net toner charge and toner throw-off are measured for each of the sample toner compositions to test the charge control capabilities of the various materials added to the toner.

Each toner sample is prepared by blending all ingredients together on the rubber compounding mill for approximately 20 minutes. Each melt is then cooled to room temperature and ground in a laboratory disk grinder to pass through a 20 mesh screen. Final grinding to a particle size less than 30 microns is accomplished in a fluid energy mill. The net toner charge is measured by mixing 6 percent of the toner with an insulating polymer-coated particulate carrier comprising an oxidized sponge iron core coated with a terpolymer of acrylonitrile-vinylidene chloride-acrylic acid as described in McCabe, U.S. Ser. No. 236,765, now U.S. Pat. No. 3,795,617 filed Mar. 21, 1972, Case B. The mixing is accomplished by placing the carrier and toner in a small paper cup which is then rolled on a roll mill for 15 minutes. The net toner charge is measured using a Faraday Cage in the following manner: a weighed portion of each of the developers is placed in an iron tube that is covered at one end with a 200 mesh screen that retains all carrier particles within the tube. The iron tube is connected in series with a capacitor to ground. An air stream is then directed through the tube, blowing toner particles off the carrier, through the 200 mesh screen at the exit end. The potential resulting on the capacitor is measured by an electrometer. The potential obtained is converted to electrical charge in microcoulombs and this figure is divided by the weight in grams of the toner that is removed from the tube, providing the net toner charge in microcoulombs per gram.

In addition to net toner charge, a test is devised to measure the toner throw-off exhibited by each of the sample toners when admixed with a particulate carrier vehicle as follows: A fixed quantity of a well-mixed developer (i.e. mixture of toner and carrier particles) is measured and placed in an open cup positioned in a de-

vice oscillating laterally through a 0.75 inch distance at 6 cycles per second for a fixed period of time. The toner throw-off of the developer mix due to the oscilla-

tion is collected on filter paper via a vacuum and weighed. The amounts so weighed are reported in Table I below in milligrams.

TABLE I

Charge Agent (outside invention)	Concentration (parts/100 parts polycarbonate)	Charge ($\mu\text{coul/g}$)	Throw-off (mg)
Control (no charge agent)	—	0.4	350.7
6% cobalt naphthenate solution	0.5	7.0	73.7
6% cobalt naphthenate solution	1.0	5.6	92.8
6% cobalt naphthenate solution	3.0	6.0	101.5
6% cobalt naphthenate solution	6.0	5.5	169.6
Heptyldimethylsulfonium bromide (HDSB)	1.0	4.8	110.4
HDSB	3.0	3.5	91.5
Tetrabutylphosphonium bromide (TBPB)	1.0	9.0	39.3
TBPB	3.0	11.2	30.0
Ethylpyridinium chloride (EPC)	1.0	10.3	12.9
EPC	3.0	8.3	22.9
Butylpyridinium chloride (BPC)	1.0	12.6	13.0
BPC	3.0	10.7	
Methylquinolinium chloride (MQC)	1.0	10.1	18.6
MQC	3.0	9.0	24.0
MQC	4.5	6.4	32.0
Acetoquat*cetyl trimethyl ammonium bromide (CTAB)	0.5	8.6	9.7
Acetoquat*CTAB	1.0	9.0	7.9
Acetoquat*CTAB	3.0	8.9	9.0
Acetoquat*cetyl trimethyl ammonium chloride (CTAC)	0.5	8.4	16.4
Acetoquat*CTAC	1.0	10.2	17.8
Dimethylphenylbenzylammonium chloride (DPBAC)	0.5	2.7	391.8
DPBAC	1.0	3.1	248.8
DPBAC	3.0	6.6	44.1
Triethylbenzylammonium chloride (TBAC)	0.5	2.3	294.9
TBAC	1.0	1.1	448.5
TBAC	3.0	0.9	159.5
Trimethylphenylammonium chloride (TPAC)	0.5	1.2	21.6
TPAC	1.0	0.3	7.2
TPAC	3.0	-0.9	3.3
Tetraethylammonium chloride (TPACL)	0.1	10.6	18.3
TPACL	0.3	12.4	14.4
TPACL	0.5	14.3	3.6
TPACL	1.0	13.0	4.2
TPACL	1.5	13.3	1.6
TPACL	3.0	12.5	5.2
TPACL	6.0	7.6	46.4 (Avg)
Tetraheptylammonium chloride (THACL)	0.3	10.1	Not available (N.A.)
THACL	0.5	14.6	N.A.
THACL	1.0	11.6	N.A.
Tetrapentylammonium hexafluorophosphate (TPAFP)	0.5	8.9	N.A.
TPAFP	1.0	9.8	N.A.
TPAFP	2.0	7.9	N.A.
Tetraethylammonium benzoate (TEAB)	1.0	11.4	4.0
TEAB	3.0	5.0	45.3
Tetraethylammonium acetate tetrahydrate (TEAAT)	0.5	7.7	2.6
TEAAT	1.0	11.4	3.4
Tetrapentylammonium bromide (TPAB)	0.25	12.2	N.A.
TPAB	0.5	15.7	N.A.
TPAB	1.0	12.3	3.7
TPAB	3.0	10.1	N.A.
Tetrabutylammonium iodide (TBAI)	0.5	13.5	8.6
TBAI	1.0	10.8	4.1
TBAI	1.5	11.5	4.9
TBAI	3.0	9.9	11.2
Tetrabutylammonium nitrate (TBAN)	1.0	11.7	4.9
TBAN	3.0	10.2	6.3

*Trademark of Aceto Chemical Co., Inc.

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EXAMPLE 2

Toners are prepared and tested according to Example 1, except that a polystyrene resin (Piccolastic D125) is substituted for the polycarbonate and 6.0 parts of the carbon black are used per 100 parts of polymer. The results obtained are given in Table II.

TABLE II

Charge Agent	Concentration (parts/100 parts Piccolastic D125)	Charge ($\mu\text{coul/g}$)	Throw-off (mg)
Control (no charge agent)	—	2.6	188.5
Tetrapentylammonium chloride (TPAC)	0.1	6.6	20.7
	0.5	8.0	16.5

These results indicate that the significant effect on charge obtained with the charge control agents of our invention is applicable to a variety of polymeric binders and is not restricted to the use of polycarbonate binders.

Electrophotographic electrostatic charge patterns obtained in the conventional manner and processed with developer compositions containing the charge control agents of our invention provide images that are dense and sharp with little or no coloration, i.e. deposition of toner particles, in non-image background areas, toner throw-off or dusting in magnetic brush processes is minimal and the prints containing the transferred images can be handled repeatedly, bent, folded and the like without causing undue flake-off of the image thereon. (See Example 3).

EXAMPLE 3

A toner with one part tetrabutylammonium nitrate and 5.7 parts Sterling FT carbon black per 100 parts resin is prepared according to Example 1. The toner is mixed with a magnetic carrier as described in Example 1 at 6% concentration. This resultant developer is placed in a magnetic brush of the general type described in U.S. Pat. No. 3,003,462. An organic photoconductor-containing element bearing a latent electrostatic charge image is passed over the magnetic brush. The toned image thus formed on the photoconductor-containing element is subsequently transferred to paper. The toned image is fused to paper with an infrared lamp. Using the above-described developer, the magnetic brush exhibits low toner throw-off. The images that are formed are sharp, of high density, and advantageously exhibit very low background coloration. The images, after fusing, exhibit good adhesion to paper.

EXAMPLE 4

A toner with 0.5 parts tetrapentylammonium chloride and 5.7 parts Sterling FT carbon black per 100 parts resin was prepared according to Example 1. The toner was mixed with a carrier described in Example 1 at 6% concentration. This resultant developer is placed in a magnetic brush of the general type described in U.S. Pat. No. 3,003,462. An organic photoconductor-containing element bearing a latent electrostatic charge image is passed over the magnetic brush. The toned image thus formed on the photoconductor-containing element is subsequently transferred to paper. The toned image is fused to paper with an infrared lamp. Using the above-described developer, the mag-

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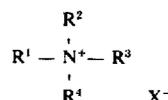
netic brush exhibits low toner throw-off. The images that are formed are sharp, of high density, and advantageously exhibit very low background coloration. The images, after fusing, exhibit good adhesion to paper.

The invention has been described in detail with particular reference to preferred embodiments thereof, but, it will be understood that variations and modifica-

tions can be effected within the spirit and scope of the invention.

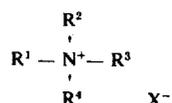
We claim:

1. A dry particulate electroscopic toner composition for use in developing electrostatic charge patterns comprising finely-divided particles comprising a resin having incorporated therein a quaternary ammonium charge control agent having the following formula:



wherein R^1 , R^2 , R^3 and R^4 represent an aliphatic hydrocarbon group having one to seven carbon atoms and X^- represents an anionic function.

2. A dry particulate electroscopic toner composition for use in developing electrostatic charge patterns comprising finely-divided particles having a particle size of from about 0.1 micron to about 100 microns, said particles comprising a resin having a melting point within the range of from about 65° to about 200°C. and having incorporated in said resin a quaternary ammonium charge control agent having the following formula:

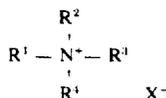


wherein R^1 , R^2 , R^3 and R^4 represent an aliphatic hydrocarbon group having one to seven carbon atoms and X^- represents an anionic function, said particles comprising about 0.1 to about 6 parts by weight charge control agent per 100 parts by weight of said resin.

3. The invention as described in claim 2 wherein said toner composition comprises a pigment or a dyestuff in an amount effective to color said toner composition.

4. A dry particulate electroscopic toner composition for use in developing electrostatic charge patterns comprising finely-divided particles having a particle size of from about 1.0 to about 30 microns, said particles comprising a styrene-containing resin having a melting point within the range of from about 65°C. to about 120°C. and having incorporated in said resin (a) a pigment or dyestuff in an amount effective to color said resin and (b) a quaternary ammonium charge control agent having the following formula:

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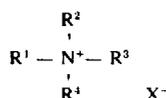
wherein R¹, R², R³ and R⁴ represent an aliphatic hydrocarbon group having one to seven carbon atoms and where X⁻ is an anionic function, said particles comprising about 0.3 to about 3.0 parts by weight charge control agent per 100 parts by weight of said resin.

5. The invention as described in claim 4 wherein R¹, R², R³ and R⁴ represent an alkyl group having from 1 to about 7 carbon atoms and wherein X⁻ is an anionic function selected from the group consisting of halides, phosphates, acetates and nitrates.

6. The invention as described in claim 4 wherein R¹, R², R³, and R⁴ are straight-chain alkyl groups having from about 3 to about 7 carbon atoms and wherein X⁻ is a halide.

7. The invention as described in claim 4 wherein R¹, R², R³, and R⁴ are straight-chain alkyl groups having from about 3 to about 7 carbon atoms and wherein X⁻ is a chloride.

8. A dry particulate electroscopic toner composition for use in developing electrostatic charge patterns comprising finely-divided particles of from about 0.1 micron to about 100 microns, said particles comprising a polycarbonate-containing resin having a glass transition temperature within the range of from about 60°C. to about 120°C. and having incorporated in said resin (a) a dyestuff or pigment in an amount effective to color said resin and (b) a quaternary ammonium charge control agent having the following formula:



wherein R¹, R², R³ and R⁴ represent an aliphatic hydrocarbon group having one to seven carbon atoms and wherein X⁻ is an anionic function.

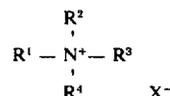
9. The invention as described in claim 8 wherein R¹, R², R³ and R⁴ represent an aliphatic group having from 1 to about 7 carbon atoms and wherein X⁻ is an anionic function selected from the group consisting of halides, phosphates, acetates and nitrates.

10. The invention as described in claim 8 wherein R¹, R², R³ and R⁴ represent an alkyl group having from about 3 to about 7 carbon atoms and wherein X is a halide.

11. A dry particulate electroscopic toner composition for use in developing electrostatic charge patterns comprising finely-divided particles of from about 1.0 to about 30 microns, said particles comprising a styrene-containing resin having a melting point within the range of from about 65°C. to about 120°C., said resin containing from about 40 to about 100 percent by weight of styrene units, from 0 to about 45 percent by weight of alkyl acrylate or alkyl methacrylate units having from 1 to about 3 carbon atoms in the alkyl moiety, and from about 5 to about 50 percent by weight of alkyl acrylate or alkyl methacrylate units having from about 6 to about 20 carbon atoms in the alkyl moiety, said resin

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having incorporated therein (a) a pigment or dyestuff in an amount effective to color said resin and (b) a quaternary ammonium charge control agent having the following formula:



wherein R¹, R², R³ and R⁴ represent an aliphatic hydrocarbon group having one to seven carbon atoms and wherein X⁻ is an anionic function, said particles comprising about 0.1 to about 6 parts by weight charge control agent per 100 parts by weight of said resin.

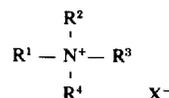
12. The invention as described in claim 11 wherein R¹, R², R³ and R⁴ represent an aliphatic group having from 1 to about 7 carbon atoms and wherein X⁻ is an anionic function selected from the group consisting of halides, acetates, phosphates, and nitrates.

13. The invention as described in claim 11 wherein said particles contain carbon black as a pigment.

14. The invention as described in claim 11 wherein R¹, R², R³ and R⁴ represent an alkyl group having from about 3 to about 7 carbon atoms and wherein X is a halide.

15. An electrographic developing composition comprising particulate magnetic carrier particles having electrostatically attractable thereto a toner composition as described in claim 1.

16. An electrographic developer composition comprising ferromagnetic carrier particles having a particle size within the range of from about 30 to about 1200 microns and having electrostatically attractable thereto dry, finely-divided toner particles having a particle size within the range of about 1.0 to about 30 microns, said toner particles comprising a resin having a melting point within the range of from about 65° to about 200°C. and having incorporated in said resin (a) a dyestuff or pigment in an amount effective to color said resin and (b) a quaternary ammonium charge control agent having the following formula:



wherein R¹, R², R³ and R⁴ represent an aromatic or an aliphatic hydrocarbon group having one to seven carbon atoms and wherein X⁻ is an anionic function, said toner particles comprising about 0.3 to about 3.0 parts by weight of charge control agent per 100 parts by weight of said resin.

17. The invention as described in claim 16 wherein said resin is a styrene-containing resin having a melting point within the range of about 65° to about 120°C. and wherein said toner particles comprise carbon black as a pigment.

18. The invention as described in claim 16 wherein said resin is a poly(carbonate)-containing resin having a glass transition temperature within the range of from about 60° to about 120°C. and wherein said toner particles comprise carbon black as a pigment.

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