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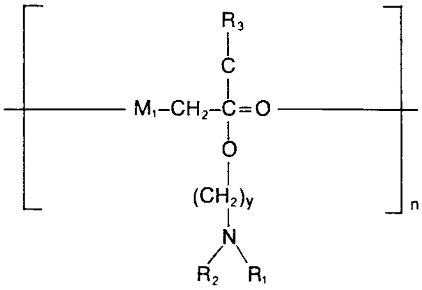
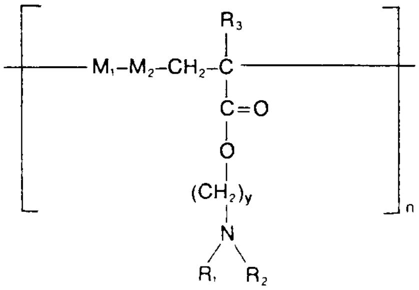
(54) **Electrophotographic toner composition.**

(57) An electrophotographic toner composition which comprises a colorant and a resin. The resin is an amine copolymer or terpolymer having the formula:



$$\left[\; M_1-CH_2-\overset{\overset{R_3}{|}}{C}(=O)-O-(CH_2)_y-N(R_2)R_1 \;\right]_n$$

or



$$\left[\; M_1-M_2-CH_2-\overset{R_3}{C}(C{=}O)-O-(CH_2)_y-N(R_1)R_2 \;\right]_n$$

wherein M_1 is a monomeric unit, such as styrene methyl methacrylate, n-butyl methacrylate, isobutyl styrene; M_2 is a similar monomeric unit different from M_1, R_1 and R_2 are independently selected from hydrogen and carbon containing radicals with from 1 to 8 carbon atoms, such as hydrocarbon and substituted hydro-carbon radicals, R_3 is hydrogen or a hydrocarbon group with from 1 to 8 carbon atoms, n is an integer between 50 and 100,000 and Y is an integer between 1 and 5, said copolymer or terpolymer being prepared by vinyl or addition polymerization.

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ELECTROPHOTOGRAPHIC TONER COMPOSITION

This invention relates to an electrophotographic toner composition which comprises a colorant and a resin.

The electrophotographic process and more specifically the xerographic process is fully described in U. S. Patent 3,635,704. In summary, in the xerographic process a plate generally comprising a conductive backing upon which is placed a photoconductive insulating surface is uniformly charged and subsequently the photoconductive surface is exposed to a light image of the original to be reproduced. The photoconductive surface is prepared in such a manner so as to cause it to become conductive under the influence of the light image in order that the electrostatic charge contained thereon can be selectively dissipated to produce a latent image which is developed by means of a variety of pigmented resin materials especially made for this purpose such as toner. It is this toner material that is electrostatically attracted to the latent image areas on the plate in proportion to the charge concentration thereof, thus in areas of high charge concentration high attraction of toner results while in areas of low charge concentration substantially no toner is attracted. This developed image can then be transferred to a final support material such as paper and affixed thereto.

There are many methods that are known for developing and fixing the resulting images, some of which are disclosed in U. S. Patent No. 3,635,704 and include for example, cascade development as described in U. S. Patent No. 2,618,552; magnetic brush development as described in U. S. Patents 2,874,063; 3,251,706; and 3,357,402; powder cloud development as described in U.S. Patent

No. 2,221,776; and touchdown development as described in U. S. Patent No. 3,166,432. The fixing can be either vapor fixing, heat fixing, pressure fixing or combinations thereof as described in U.S. Patent No. 3,539,161. Modern electrostatographic reproducing apparatuses which are capable of producing copies at extremely high rates can employ radiant flash fusing as this seems to be the best method for affixing images in such environments. The energy which is emitted in the form of electromagnetic waves is instantly available and requires no intervening medium for its propogation.

The type of toner material that is used in a development system is very important as not only is the image quality a consideration, but cleaning and damage to machine components is a factor that must be contended with. After forming a powder image on the electrostatic latent image during the development step as explained herein, the powder image can be electrically transferred to the support surface by means of a corona generating device as described for example in U.S. Patent No. 2,777,957. Specifically, transfer is effected by such a device by imparting an electrostatic charge to attract the powder image from the drum to the support surface. The polarity of the charge required to affect the transfer of the image depends upon the visual form of the original copy relative to the reproduction as well as the electroscopic characteristics of the developing material employed to accomplish development. Thus, when a positive reproduction is to be obtained from a positive original it is conventional to employ a positive polarity corona to affect the transfer of a negatively charged toner image to a support surface. When a positive reproduction from a negative original is desired normally there is used a positively charged developing material which is repelled by the charged areas on the plate to the discharged areas thereon to ses

form a positive image which may be transferred by negative polarity corona. Additionally, of course, the type of charge that is to be imparted to the toner material will depend on the charge on the photoconductive surface, thus if such charge is negative one would want a positive charge on the resulting toner or if such a charge is positive one would want a negative charge on the resulting toner.

It is known to modify the developer composition containing toner so as to achieve optimum copy quality consistently without adversely affecting the imaging system involved. For example, it has been found to be an advantage to modify the properties of the toner so that a uniform stable high net electrical charge may be imparted to the toner powder material. Numerous methods and materials for modifying the surface properties of toner have been proposed including for example the addition of various dyes, amines, quaternary ammonium compounds, all of which have been used as charge controlling agents in electrophotographic toners. While these additives are somewhat effective in controlling the toner charges, the additives used can adversely affect the system in that, for example, charge could migrate from the interior of the toner to the surface due to energy differences which results in causing the toner to change its charge property and to be less attracted to the electrophotographic latent images in some situations. Also, these additives are either water soluble or moisture sensitive; thus adversely affecting the toner and the quality of the image. Further, such additives are difficult to disperse or dissolve uniformly in the toner which results in particle to particle non-uniformity and wide distribution of electrical charges.

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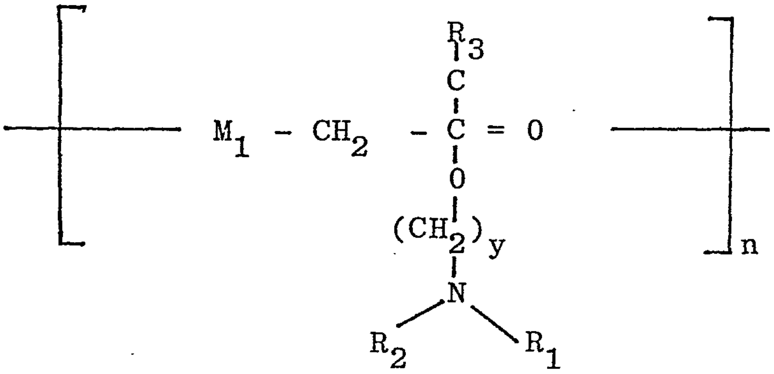
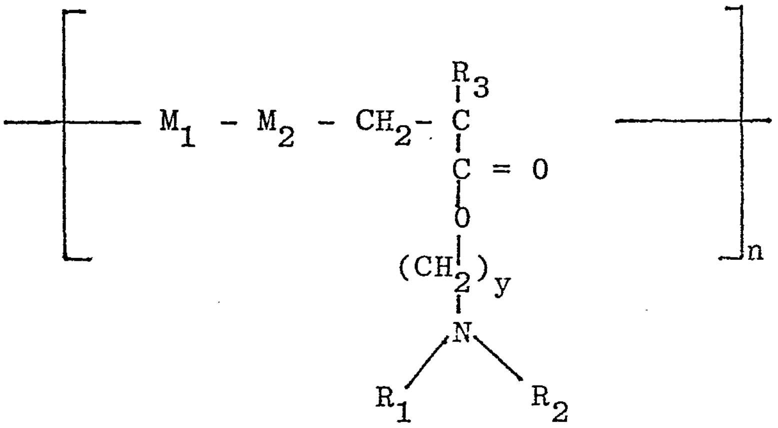
The invention as claimed is intended to provide a toner composition which is positively charged and which does not require the use of an additive to obtain such a charge. This toner composition is characterised by the inclusion of a resin which is in an amine copolymer or terpolymer having the formula:



$$\left[M_1 - CH_2 - \overset{\substack{R_3 \\ | \\ C \\ |}}{\underset{\substack{| \\ O \\ | \\ (CH_2)_y \\ | \\ N \\ \diagup \quad \diagdown \\ R_2 \qquad R_1}}{C}} = O \right]_n$$

or



$$\left[M_1 - M_2 - CH_2 - \overset{\substack{R_3 \\ |}}{\underset{\substack{| \\ C = O \\ | \\ O \\ | \\ (CH_2)_y \\ | \\ N \\ \diagup \quad \diagdown \\ R_1 \qquad R_2}}{C}} \right]_n$$

wherein M_1 is a monomeric unit, M_2 is a monomeric unit different from M_1, R_1 and R_2 are independently selected from hydrogen, carbon containing radicals, hydrocarbon and substituted hydrocarbon radicals, R_3 is hydrogen or a hydrocarbon group, n is an integer between 50 and 100,000 and Y is an integer between 1 and 5, said copolymer or terpolymer being prepared by vinyl or addition polymerization.

The toner compositions of the invention have the advantages that they provide improved toners having the desired charge characteristics that are permanently retained and which allow the development of images of high quality especially when a negative charge is present on the photoreceptor used.

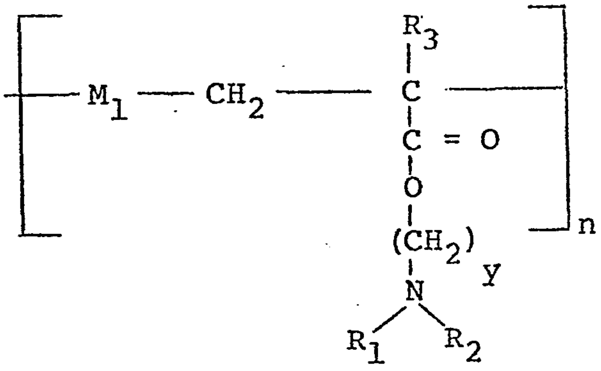
Toner composition in accordance with the invention will now be described in more detail.

Generally the colorant which can be a carbon black, magnetite or colorant pigment is present in amounts of from about 1 to about 70 percent by weight while the resin is present in amounts of from about 30 to 99 percent by weight. In order to achieve optimum results it is preferred that the colorant be present in amounts of from 4 to about 50 percent based on the weight of toner and the resin be present in amounts of from 50 to about 96 percent by weight.

Any suitable pigment or dye may be employed as the colorant including for example carbon black, nigrosine dye, aniline blue, Calco Oil Blue, chrome yellow, ultramarine blue, DuPont Oil Red, methylene blue chloride, phthalocyanine blue, Rose Bengal, iron oxides such as Mapico Black, Mapico Yellows, Mapico Reds, Mapico Browns, Mapico Tans, and mixtures thereof. The pigment or dye should be present in the toner in a sufficient quantity to render it colored so that it will form a clearly visible image on the recording surface and generally as indicated above the percent of colorant present varies from about 1 to about 70 percent. Thus for example where conventional xerographic copies of typed documents are desired the toner may comprise a black pigment such as carbon black or magnetite.

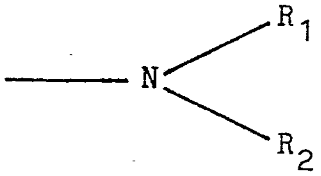
Numerous types of resin materials may be used for preparing toner compositions of the present invention with the provision that the resulting product contains an amino group which causes the toner to be positively charged in one preferred embodiment thus allowing it to be used in those situations where the photoreceptor, especially an organic photoreceptor, is negatively charged.

The resin of the invention may be illustrated by an amine copolymer having the following structure:



wherein M_1 is a monomeric unit such as styrene methyl methacrylate, n-butyl methacrylate, isobutyl styrene; R_1 and R_2 are as defined below; R_3 is hydrogen or a hydrocarbon group, such group containing from about 1 to about 8 carbon atoms and including for example, methyl, ethyl, propyl, isopropyl, hexyl, octyl; n is an integer of from about 50 to 100,000; and y is an integer of from about 1 to 5. The terpolymer would be of similar structure with the addition of an M_2 grouping, $-M_1-M_2-CH_2$ wherein M_2 is usually a different monomeric unit such as n-butyl methacrylate.

The resin contains an amino group such as a primary, second or tertiary group of the formula



wherein R_1 and R_2 are independently selected from hydrogen, carbon containing radicals, hydrocarbon and substituted hydrocarbon groups. R_1 and R_2 could be bonded to the nitrogen-N through the same carbon atom ($=CH_2$) or through different carbon atoms ($N<^{CH}_{CH}$). The hydrocarbon or substituted hydrocarbon can be aliphatic or aromatic with the aliphatic group containing from 1 to about 8 carbon atoms including for example, methyl, ethyl, propyl, isopropyl, hexyl, and octyl. Examples of substituents in the hydrocarbon group include hydroxyl, halo chloride, bromide, nitro, amino, sulfonyl, while examples of aromatic groups include phenyl, benzyl phenyl, and heterocyclic such as nitrogen containing aromatics.

Illustrative examples of copolymers and terpolymers containing the amino group include styrene t-butyl amino ethyl methacrylate, styrene n-butyl methacrylate, t-butyl amino ethyl methacrylate, dimethylamino ethyl methacrylate.

The resins of the invention are vinyl or addition type copolymers or terpolymers containing amino groups. Typical of such vinyl monomeric units include the following monomers and monomers containing amino groups: styrene; p-chlorostyrene; vinyl naphthalene; ethylenecally unsaturated mono-olefins such as ethylene, propylene, butylene, isobutylene and the like; vinyl esters such as vinyl chloride, vinyl bromide, vinyl fluoride, vinyl acetate, vinyl propionate, vinyl benzoate, vinyl butyrate and the like; esters of alphamethylene aliphatic monocarboxylic acids such as methyl acrylate, ethyl acrylate, n-butylacrylate, isobutyl acrylate, dodecyl acrylate, n-octyl acrylate, 2-chloroethyl acrylate, phenyl acrylate, methyl-alpha-chloroacrylate, methyl methacrylate, ethyl methacrylate, butyl methacrylate and the like; acrylonitrile, methacrylonitrile, acrylamide, vinyl ethers such as vinyl methyl ether, vinyl isobutyl ether, vinyl ethyl ether, and the like; vinyl ketones such as vinyl methyl ketone, vinyl hexyl ketone, methyl isopropenyl ketone and the like; vinylidene halides such as vinylidene chloride, vinylidene chlorofluoride and the like; and N-vinyl compounds such as N-vinyl pyrrol, N-vinyl carbazole, N-vinyl indole, N-vinyl pyrrolidone, N-vinyl pyridine, n-butylamino ethyl methacrylate, t-butylamino ethyl methacrylate, dimethyl amino ethyl methacrylate, and the like; and mixtures thereof.

The addition polymerization technique employed embraces known polymerization techniques such as free radical, anionic and cationic polymerization processes. Any of these vinyl resins may be blended with one or more other resins if desired, preferably other vinyl resins which insure good triboelectric stability and uniform resistance against physical degradation.

Where carrier materials are employed with the toner compositions of the present invention in cascade and magnetic brush development, the carrier particles employed may be electrically conductive, insulating, magnetic or non-magnetic, as long as the carrier particles are capable of triboelectrically obtaining a charge of opposite polarity to that of the toner particles so that the toner particles adhere to and surround the carrier particles. In developing a positive reproduction of an electrostatic image, the carrier particle is selected so that the toner particles acquire a charge having a polarity opposite to that of the electrostatic latent image so that toner deposition occurs in image areas. Alternatively, in reversal reproduction of an electrostatic latent image, the carriers are selected so that the toner particles acquire a charge having the same polarity as that of the electrostatic latent image resulting in toner deposition in the non-image areas. Typical carrier materials include: sodium chloride, ammonium chloride, aluminum potassium chloride, Rochelle salt, sodium nitrate, aluminum nitrate, potassium chlorate, granular zircon, granular silicon, methyl methacrylate, glass, steel, nickel, iron, ferrites, ferromagnetic materials, silicon dioxide and the like. The carriers may be employed with or without a coating. Many of the foregoing and typical carriers are disclosed in U. S. Patents 2,618,441; 2,638,552; 3,591,503 and 3,533,835 directed to electrically conductive carrier coatings, and U. S. Patent 3,526,533 directed to methyl terpolymer coating carriers which are the reaction products or organo silanes, silanols or siloxanes with unsaturated polymerizable organic compounds (optimum among those disclosed are terpolymer coatings achieved with a terpolymer formed from the addition polymerization reaction between monomers or prepolymers of: styrene, methylmethacrylate and unsaturated organo silanes, silanols or siloxanes); and nickel berry carriers as disclosed in U. S. Patents 3,847,604 and 3,767,598. Nickel berry carriers are modular carrier beads of nickel characterized by a surface of recurring recesses and protrusions giving the particles a relatively large external surface area. An ultimate coated carrier particle diameter between about 50 microns to about 1000 microns is preferred because the carrier particles then possess sufficient density and inertia to avoid adherence to the electrostatic images during the cascade development process. The carrier may be employed with the toner composition in any suitable combination, generally satisfactory results have been obtained when about 1 part toner is used with about 10 to about 200 parts by weight of carrier.

The toners of the present invention may be utilized in systems such as powder cloud development, cascade development, single component touchdown development and other types of development systems.

The toner compositions of the present invention can be prepared by any well known toner mixing and combination technique for example, the ingredients may be thoroughly mixed by blending, mixing and milling the components and thereafter micropulverizing the resulting mixture. Another well known technique for forming toner particles is to spray-dry a ball milled toner composition comprising a colorant, a resin and a solvent. The toner compositions of the present invention can be used to develop electrostatic latent imageson any suitable electrostatic surface capable of retaining charge including conventional photoconductors such as inorganic or organic photoconductive materials. Some typical materials include sulfur, selenium, zinc sulfide, zinc oxide, cadmium sulfide, polyvinyl carbazole, 4 dimethyl amino benzylidene, 3 amino carbazole, polyvinyl carbazole, tri-nitrofluoronone, charge transfer complexes, phthalocyanines, and the like.

It is important to note that no additives are being supplied in or to the toner of the present invention, that is no material is being supplied to the developer rather the resin is prepared in such a manner so as to contain amino functionality which results in the property desired. The results as demonstrated by the working examples will aid as will be more fully established in the working examples that follow.

The following examples are being supplied to further illustrate the invention. Parts and percentages are by weight unless otherwise indicated.

The triboelectric charge of the developer was measured by the following procedure. One hundred (100) parts of the coated carrier and 3 parts of the toner were placed in an 8 oz. glass jar. The jar containing the developer was roll mixed at a linear speed of 90 ft/min for a specific time. The developer was placed in a stainless steel Faraday cage with a 35 micron screen. The triboelectric charge was measured by blowing off the toner from the developer, using an electrometer which is connected to the Faraday cage.

EXAMPLE I

Toner A comprised of 6 percent Regal 330 carbon black from Cabot Corporation and 94 percent of a copolymer resin was prepared by Banbury blending followed by mechanical attrition. The copolymer resin was prepared by polymerizing 65 percent styrene and 35 percent n-butyl methacrylate using benzyl peroxide as an initiator. The triboelectric charge of this toner against a 0.35 percent PFA (perfluor alkoxy fluoro polymer from duPont Co.) coated Hoeganaes carrier was measured by the procedure outlined above with the following results. The word 'tribo' is used hereafter to denote triboelectric charge.

Roll Mixing Time	Toner Tribo µc/g (micro coulomb per gram of toner)
10 min	+17
60 min	+7
2 hr	+3
4 hr	-3

The tribo decreased rapidly as the mixing time was increased. After 4 hours of mixing, the charge of the toner changed from positive to negative, indicating it was not a stable developer.

EXAMPLE II

Toner B which is comprised of 6 percent Regal 330 carbon black and 94 percent of Terpolymer 1 resin was prepared by Banbury/jetting. The Terpolymer 1 resin of this toner was prepared by polymerizing 60 percent styrene, 38 percent n-butyl methacrylate, and 2 percent t-butylamino ethyl methacrylate using benzoyl perioxide as an initiator. The triboelectric measurements of this toner against a 0.35 percent PFA (perfluoro alkoxy fluoro polymer from DuPont Co.) coated Hoeganaes carrier were as shown in the following table:

Roll Mixing Time	Toner Tribo µ c/g (micro coulomb per gram of toner)
5 min	+18
10 min	+18
1 hr	+18
4 hr	+20
24 hr	+15

The charging rate of this toner was rapid and the tribo was rather high and stable.

EXAMPLE III

Toner C comprising 6 percent Regal 330 carbon black and 94 percent Terpolymer 2 resin was prepared by Banbury/jetting. The Terpolymer 2 resin of this toner was prepared by polymerizing 60 percent styrene, 36 percent n-butyl methacrylate, and 4 percent t-butylamino ethyl methacrylate using benzoyl peroxide as initiator. The tribos of this toner against a 0.35 percent PFA (perfluoro alkoxy fluoro polymer from duPont Co.) coated Hoeganaes carrier were as shown in the following table:

Roll Mixing Time	Toner Tribo μ c/g (micro coulomb per gram of toner)
5 min	+21
10 min	+21
1 hr	+23
4 hr	+24
24 hr	+24

The toner displayed fast charging rate and high and stable tribo.

EXAMPLE IV

Toner D comprising 6 percent Regal 330 carbon black and 94 percent Terpolymer 3 resin was prepared by Banbury/jetting. The Terpolymer 3 resin of this toner was prepared by polymerizing 60 percent styrene, 34 percent n-butyl methacrylate and 6 percent t-butyl amino ethyl methacrylate using benzoyl peroxide as initiator. The tribo of this toner against a 0.35 percent PFA (perfluoro alkoxy fluoro polymer from duPont Co.) coated Hoeganaes carrier were as shown in the following table:

Roll Mixing Time	Toner Tribo μ c/g (micro coulomb per gram of toner)
5 min	+26
10 min	+26
1 hr	+26
4 hr	+28
24 hr	+27

The toner displayed fast charging rate, high and stable tribo.

EXAMPLE V

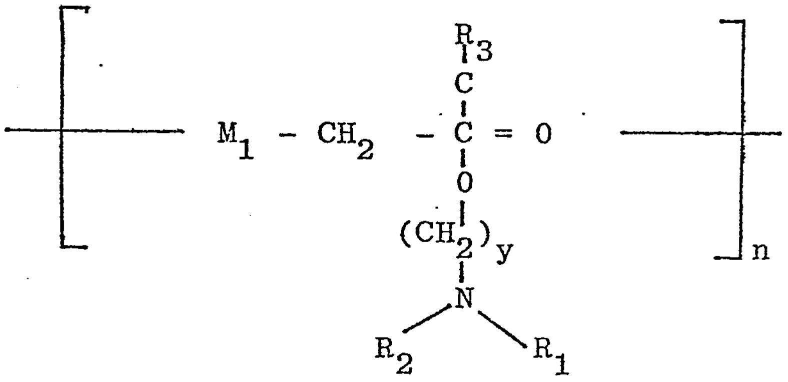
Toner E comprising 6 percent Regal 330 carbon black and 94 percent Terpolymer 4 resin was prepared by Banbury/jetting. The Terpolymer 4 resin of this toner was prepared by polymerizing 50 percent methyl methacrylate, 45 percent n-butyl methacrylate, and 5

Roll Mixing Time	Toner Tribo µc/g (micro coulomb per gram of toner)
5 min	+14
10 min	+12
1 hr	+12
4 hr	+13
24 hr	+17

The toner displayed fast charging rate, high and stable tribo against uncoated steel carrier.

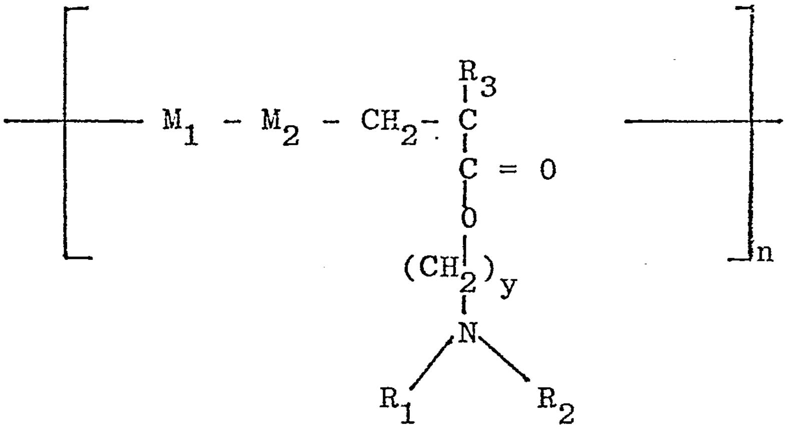
Claims:

1. An electrophotographic toner composition comprising a colorant and a resin, characterised in that the resin is an amine copolymer or terpolymer having the formula:



$$\left[- M_1 - CH_2 - \underset{\underset{\underset{\underset{\underset{R_2 \quad R_1}{N}}{|}}{(CH_2)_y}}{|}}{\underset{O}{\underset{|}{\overset{\overset{\overset{R_3}{|}}{C}}{\overset{|}{C}}}}} = O - \right]_n$$

or



$$\left[- M_1 - M_2 - CH_2 - \underset{\underset{\underset{\underset{\underset{\underset{R_1 \quad R_2}{N}}{|}}{(CH_2)_y}}{|}}{O}}{\underset{|}{\underset{C = O}{\underset{|}{\overset{\overset{R_3}{|}}{C}}}}} - \right]_n$$

wherein M_1 is a monomeric unit, M_2 is a monomeric unit different from M_1, R_1 and R_2 are independently selected from hydrogen, carbon containing radicals, hydrocarbon and substituted hydrocarbon radicals, R_3 is hydrogen or a hydrocarbon group, n is an integer between 50 and 100,000 and Y is an integer between 1 and 5, said copolymer or terpolymer being prepared by vinyl or addition polymerization.

2. A toner composition in accordance with Claim 1 wherein a terpolymer resin is used containing tertiary butyl amino ethyl methacrylate.

3. A toner composition in accordance with Claim 1 wherein a terpolymer resin is used containing n-butyl amino ethyl

methacrylate.

4. A toner composition in accordance with Claim 1 wherein a terpolymer resin is used containing dimethylamino ethyl methacrylate.

5. A toner composition in accordance with Claim 1 wherein R_1 and/or R_2 is benzyl phenyl.

6. A method for producing an electrophotographic image comprising forming an electrostatic latent image on an image bearing material followed by development with the toner composition of any one of claims 1 to 5, transferring the developed image to a paper substrate, and permanently forming the image thereon.

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European Patent Office

EUROPEAN SEARCH REPORT

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Application number

EP 79 30 0655

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim
X	CHEMICAL ABSTRACTS, Vol. 81, no.6, August 12, 1974, abstract no. 31850d, page 440, column 1 COLUMBUS, OHIO (US) TOMARI, SEIJI: "Electrographic dry developer toner containing charge controlling polymers" & JP - A - 73 102 633 (CANON K.K.) * the entire abstract * ---	1-4,6
X	GB - A - 1 352 804 (KONISHIROKU PHOTO IND.) * claims; page 2, lines 23-75; examples * ---	1-6
	DE - A - 1 597 861 (K.K. RICOH) * claims * ---	1-6
	DE - A - 1 772 439 (K.K. RICOH) * claims * ---	1-6
	US - A - 3 968 044 (Y. TAMAI) * the abstract; claims; column 2, lines 26-43 * ---	1,6
	DE - A - 2 512 112 (HITACHI CHEM.) * the claims * ---------	1-6

CLASSIFICATION OF THE APPLICATION (Int. Cl.²)

G 03 G 9/08

TECHNICAL FIELDS SEARCHED (Int.Cl.²)

G 03 G 9/08

CATEGORY OF CITED DOCUMENTS

X: particularly relevant
A: technological background
O: non-written disclosure
P: intermediate document
T: theory or principle underlying the invention
E: conflicting application
D: document cited in the application
L: citation for other reasons

&: member of the same patent family, corresponding document

☑ The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
The Hague	02-08-1979	VANHECKE

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