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Parent et al.

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[45] **Oct. 29, 1974**

[54] FORON YELLOW AS A TONER COLORANT

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[51] **Int. Cl.** **G03g 13/08** G03g/9/02
[58] **Field of Search** .... 117/17.5; 96/1 R, 1 SD, 1.2; 252/62.1; 8/4; 260/37 C, 41 C

[56] **References Cited**

UNITED STATES PATENTS

1,059,571	4/1913	Schmidlin	260/510
1,618,415	2/1927	Ellis	8/24
3,345,293	10/1967	Bartoszewicz et al.	252/62.1
3,594,110	7/1971	Happe et al.	8/4

OTHER PUBLICATIONS

Modern Plastics Encyclopedia, 1965, pgs. 417–424, Coloring Plastics, by Simpson.
Colour Index, Third Edition, Vol. 2, pgs. 2483, 2491, 2502.

Primary Examiner—Michael Sofocleous

[57] ABSTRACT

A dye colorant for use in electrophotography as a toner material is disclosed. Such dye toner systems are found to have excellent tinctorial strength and triboelectric properties among others, which render them extremely suitable for use in electrophotographic imaging processes. These toners alone and in combination with carriers as developers as employed in electrophotographic processes are also disclosed.

13 Claims, No Drawings

FORON YELLOW AS A TONER COLORANT

BACKGROUND OF THE INVENTION

This invention relates to imaging systems, and more particularly, to improved xerographic developing materials, their manufacture, and use.

Electrostatography, that branch of the imaging art which relates to the formation and utilization of latent electrostatic charge patterns to record and reproduce patterns in visible form is well known in the art. When a photoconductor is employed to form these electrostatic latent images by first charging and then selectively exposing the photoconductive layer, this imaging method is referred to as electrophotography and more commonly known as xerography, the basic techniques of which are disclosed in U.S. Pat. No. 2,297,691. The latent electrostatic images thus formed may be developed or rendered visible by deposition of a finely divided electroscopic material referred to in the art as toner. The image thus obtained may be utilized in a number of ways, for example, the image may be fused or fixed in place or transferred and then fixed to a second surface.

Electrography, the other broad general branch of electrostatography, generally divided into two broad sectors which are referred to as xeroprinting and electrographic or TESI recording, does not employ a photoresponsive medium, the charging and selective discharging thereof to form its latent electrostatic image. Xeroprinting, the electrostatic analog of ordinary printing, is more fully described in U.S. Pat. No. 2,576,047 to Schaffert. TESI imaging or transfer of electrostatic images, more fully described in U.S. Pat. No. 2,285,814, involves the formation of an electrostatic charge pattern conforming to a desired reproduction on a uniform insulating layer by means of an electrical discharge between two or more electrodes on opposite sides of the insulating medium. The lines of force generated by the latent electrostatic image are employed to control the deposition of the toner material to form an image. Various developers both powder and liquid and developing systems are well known to those skilled in the art including cascade development as disclosed in U.S. Pat. No. 2,618,552 to E. N. Wise; magnetic brush development as generally described in U.S. Pat. No. 2,874,063; powder cloud development as generally described in U.S. Pat. No. 2,784,109; touchdown development described in U.S. Pat. No. 3,166,432; and liquid development as described in U.S. Pat. No. 2,877,133 among others. These development systems, though they enjoy widespread use for black and white reproductions, may also be employed in other colors and combinations of colors, for example a trichromatic color system of either the additive or subtractive color formation types. In full color systems at least three different colors must be employed to synthesize any other desired color which involves generally the formation of at least three color separation images and their combination in registration with each other to form a color reproduction of the original. Thus, in any of the electrostatographic recording systems at least three different latent electrostatic images must be formed, developed with different color toners and combined to form the final image. For example, in color xerography an electrostatic latent image resulting from exposure to a first primary color may be formed on the photoconductive layer developed with a toner complementary to the primary color. In a similar fashion, succeeding developments of electrostatic latent images corresponding to primary colors are accomplished with complementary toners. When exposing through color separation negative, the toner is the complement of the radiation of exposure.

In a three color electrophotographic system which employs superimposed color images, it is necessary that the toners be quite transparent except for the underlying one so as not to obscure the different colored toner images below it and that each toner have sufficient color saturation at the same time and brightness to satisfy the colormetric requirements for three color synthesis of natural color images. As can be appreciated, these requirements are virtually diametrically opposed further complicated by an additional requirement that when all the toners are combined, they produce a deep black. It has sometimes been found that in order to produce deep blacks in a color system that it is required to superposition four different colored images including a black registered image. Additional problems generally arise when inorganic pigments are used as the coloring material either in printing inks or electrophotographic toners since it is difficult to achieve proper color balance and saturation while at the same time keeping the colors transparent. When employing inorganic pigments, the range of colors available is relatively narrow and these pigments are found to impart opacity to the materials to which they are added even in relatively small amounts.

Bartoszewicz et al in U.S. Pat. No. 3,345,293 teaches colored electrophotographic toners comprising substantially transparent resin particles containing organic dye pigments. These materials are stated to be advantageous in their use over prior art materials in that they are more resistant to bleeding of color upon toner fusing and they are specifically adaptable for use in three color electrophotographic processes since their colors are yellow, cyan, magenta, and their mixtures in pairs produce blue, red, and green while the three toners together produce a black. Notwithstanding the apparent advantages of the Bartoszewicz et al toners, there are nevertheless disadvantages connected with these specific toners, specifically in the case of the yellow toner when employed in an automatic electrophotographic machine. The yellow colorant as advanced by Bartoszewicz, et al, consists essentially of from about 0.92 to about 1.08 parts by weight of 3,3′-dichloro, 4′-bis(2″-acetyl-2″-azo-o-acetotoluidide)biphenyl per 10 parts by weight of a substantially transparent resin. The problems in employing this colorant reside in its inability to disperse substantially uniformly in transparent resin materials and more significantly the undesirable triboelectric properties which result from its use causing poor images of low contrast and low machine life. It is found that the triboelectric properties of the resulting toner material are not maintained under conditions where the toner is exposed to mechanical abrasion, high temperatures, and high ambient humidity conditions, all of which are common in electrophotographic machines. This results in a number of problems including poor transfers from the drum surface to the copy sheet as well as maintaining cleanliness of the drum. More specifically, it is found that in electrophotographic machine use this toner impacts on its carrier further degrading the already existing undesirable triboelectric relationship and thereby adversely effecting machine performance.

In some cases it is highly desirable to employ a dye as opposed to a pigment as a developer in an electrophotographic imaging process. The tinctorial strength in a yellow dye-colorant system is not dependent on the degree of dispersion as in the pigment-colorant system. In dye systems dispersion is almost molecular, i.e. a mono dispersion, so that the dye itself is "dissolved" in a matrix resulting in an optimum color value as opposed to being dispersed as in the case of pigments. There is, therefore, a continuing need demonstrated for the discovery and application of yellow dye-color systems for use as developers in electrophotographic imaging processes.

It is, therefore, an object of this invention to provide a dye toner material which overcomes the above noted disadvantages.

Another object of this invention is to provide a dye colorant to be used in combination with a resin material as a toner for use in color imaging.

Still another object of this invention is to provide a novel electrostatographic dye-toner system.

Yet another object of this invention is to provide a novel, transparent dye-toner system.

Yet still another object of this invention is to provide a novel, transparent dye toner which may be employed in a trichromatic color synthesis of either the additive or subtractive color formation types.

Again, another object of this invention is to provide a novel electrographic developer.

Yet still another object of this invention is to provide a novel dye-toner material which possesses superior triboelectric properties and results in superior reproduction and long machine life.

Again another object of this invention is to provide a novel dye toner wherein the dye colorant disperses substantially uniformly in a resin material.

It is still another object of this invention to provide a dye toner which maintains its triboelectric properties under conditions of continuous use in an automatic electrophotographic imaging device.

Still another object of this invention is to provide a novel dye toner which transfers easily and practically completely from a drum surface to a copy sheet.

A further object of this invention is to provide a relatively pure yellow toner of a desirable shade and tone.

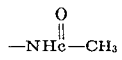
A still further object of this invention is to provide an electrophotographic process employing a novel yellow dye-toner system.

Still a further object of this invention is to provide an electrophotographic process employing a novel orange dye-toner system.

Yet still another object of this invention is to provide an electrophotographic imaging process employing a novel brown dye-toner system.

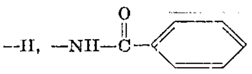
These and other objects are accomplished, generally speaking, by providing a novel dye-toner system comprising dye colorant and a resin material or materials, said colorant comprising a compound satisfying the following formula:

where R_{1-6} = —Cl, —Br, —F, —NO_2,



$-NH\overset{O}{\overset{\parallel}{C}}-CH_3$

or other acylamides,

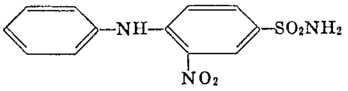


and other aryl carboxamides. —OCH_3 and other alkyl or aryl ethers, —CH_3 and other alkyl groups,

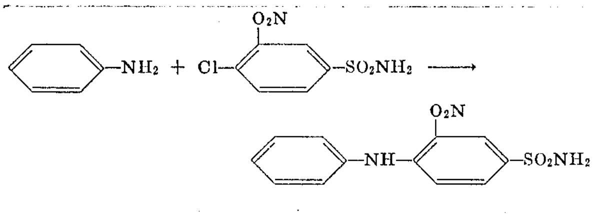
and other aryl groups both substituted and unsubstituted, —CN, —OH, —NH_2, —$NHCH_3$, and other mono and disubstituted alkyl and aryl substituted amines, —SO_2NH_2, —SO_2NH—CH_3 and other mono and disubstituted alkyl and aryl sulfonamides, —COOH, —$COOCH_3$ and other alkyl and aryl esters.

Although all combinations of the above substituents may be possible, it is obvious that steric inhibition of bulky substituents in the R_1, R_3, R_4, R_6 positions will make synthesis difficult. These constraints are familiar to those skilled in the art.

A dye of this type known as Foron Yellow, classified in the Color Index as CI Disperse Yellow 33 having the structure



may be produced employing any suitable technique. For example, a one-step condensation of aniline with 4-chloro-3-nitrobenzenesulfonamide may be performed, the reaction generally being carried out at elevated temperatures in an aqueous system containing an acid binding agent to pick up the hydrochloric acid formed. The reaction proceeds as follows:



Other compounds of this general type are Disperse Yellow 42 CI (Color Index) 10338 which may be prepared as indicated in the art (P. Fischer, BER, 24, 3794 (1891)); Disperse Yellow 14 CI 10340 (synthesized as indicated in U.S. Pat. No. 1,618,415); Disperse Yellow 1 CI 10345 (the synthesis for which appears in U.S. Pat. No. 1,618,415); SRA Fast Golden Yellow XII CI 10336 prepared through a condensation of parachloroaniline and 1-chloro-2-nitrobenzene; Disperse Yellow 26, SRA Fast Yellow X CI 10348 prepared by condensing aniline and 1,4-dichloro-2-nitrobenzene; Disperse Orange 15 CI 10350 (prepared as in U.S. Pat. No. 1,618,415); Disperse Yellow 9 CI 10375 (prepared as in U.S. Pat. No. 1,618,415); Cellete Brown R CI 10390 prepared by condensing N-(P-aminophenyl)-Nmethyltaurine with one chloro-2,4,6-trinitrobenzene, and CI 10385 (prepared as in U.S. Pat. No. 1,059,571) among others.

These colorants are distinctly different and superior to known pigment colorants of the same color since they possess the advantages stated before, i.e., tinctorial strength which is not dependent on dispersion and dispersibility which is almost molecular. Moreover, the striking difference between these dye colorants and other prior art dye colorants resides in their superior electrical properties, more specifically their triboelectric properties or tribo when combined with an appropriate electrophotographic resin, which render these colorants extremely suitable for use in electrophotographic toners and/or developers.

Upon an extended use of machine testing, conventional black toners tend to drop triboelectrically in steps until they reach the final failure level after which imaging is difficult if not impossible. These steps are not evident in prior art yellow toner-life studies such as the Bartoszewicz et al yellow toner, since these toners exhibit a steady and extreme drop in trobo resulting in shortened machine life and poor machine performance. The colorants of the instant invention, for example Foron Yellow toner compositions, on the other hand, have exhibited very stable tribo values within a well defined range with acceptable copy quality and operational characteristics over a test run of 25,000 prints. These colorants, more specifically the Foron Yellow colorant, exhibit high triboelectric characteristics which are illustrated in Table I as follows:

Print No.	Toner Conc. (%)	Tribo us/gm	Image Density (1.2)	Photoreceptor Voltages		Stability Product (grams)	Vacuum Pressure (in H_2O)	Temp. °F	Humidity %	Degree of Impaction mg/gm	Developer Running Time	
				V_o	V_b						min.	hr.
Init.	1.35	8.26	0.95			11.15		70	28			
500	1.47	10.90	0.91			16.02		70	28			
1K	1.50	14.30	0.91			21.45		70	28			
1.5K	2.12	11.54	0.86			24.46		73	27			
2K	1.97	12.93	0.92			25.46		73	27			
2.5K	1.29	20.05	0.91			25.87		70	29			
3K	1.18	13.73	0.93			16.20		70	29			
3.5K	1.64	7.23	0.91			11.84		70	29			
4K	0.93	13.32	0.90			13.05		70	27			
4.5K	1.49	12.50	0.91			18.63		70	27			
5K	1.33	10.28	0.88			13.67		70	27			
5.5K	1.23	11.96	0.90			14.71		70	27			
6K	1.69	11.41	0.92			19.28		73	27			
6.5K	1.66	15.30	0.88			25.40		73	28			
7K	2.07	15.62	0.89			32.33		73	28			
7.5K	2.54	14.00	0.89			35.55		71	33			
8K	2.26	14.08	0.92			31.82		72	32			
8.5K	1.94	14.73	0.89			28.58		72	32			
9K	1.47	12.76	0.90			18.75		72	32			
9.5K	1.25	12.46	0.91			15.57		73	30			
10K	1.83	9.47	0.88			17.34		72	30			
10.5K	1.49	11.01	0.90			19.87		72	30			
11K	1.86	10.08	0.92			18.65		71	31			
11.5K	1.65	10.28	0.95			16.96		71	31			
12K	1.40	10.61	0.89			14.85		71	34			
12.5K	1.46	11.09	0.92			16.20		70	44			
13K	1.49	5.90	0.89			13.26		72	52			
13.5K	1.35	9.28	0.89			12.53		70	30			
14K	1.27	9.20	0.88			11.69		70	30			
14.5K	1.62	6.80	0.93			11.02		70	31			
15K	1.39	8.03	0.89			11.16		72	32			
16K	1.54	8.50	0.91			13.09		70	38			
17K	1.11	9.86	0.88			10.95		70	33			
18K	1.53	7.98	0.87			12.21		70	30			
19K	1.27	8.13	0.91			10.32		70	40			
20K	1.41	6.18	0.91			8.72		70	36			
21K	1.41	5.63	0.91			7.94		70	31			
22K	1.12	7.87	0.86			8.82		70	31			
23K	1.69	4.81	0.88			8.13		73	31			
24K	1.51	4.73	0.91			7.19		70	28			
25K	1.49	5.13	0.88			7.65		74	27			

In a Xerox 720 copier, a conventional automatic electrophotographic imaging device, under controlled conditions colorants such as the benzidene yellow colorant, as taught by Bartoszewicz, et al, in U.S. Pat. No. 3,345,293, were seen to have a machine life of 1,400 prints, two conventionally employed black toners had useful lives of 4,200 and 9,000 prints whereas the Foron Yellow dye colorant of the instant invention exhibited a useful life of over 25,000 prints with no apparent adverse effects. Thus, it is readily illustrated that when prior art colorants including the yellow colorant of Bartoszewicz, et al, are combined with suitable resins to optimize their respective performances and employed in the same machine under identical conditions, the colorant of the instant invention exhibits surprisingly better performances and longer machine life.

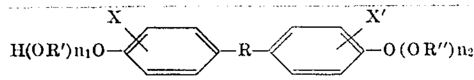
This data clearly illustrates the suitability of Foron Yellow for runs in an electrophotographic imaging device up to 25,000 prints.

Any suitable resin material may be used for the toner compositions of the present invention. As previously stated, substantially transparent resins are preferred when the toner is to be used in a three color electrophotographic system. Although any substantially transparent resin material may be utilized as the resin component of this toner, it is preferable that resins having other desirable properties be utilized in this invention. Thus, for example, it is desirable that a resin material be used which is a non-tacky solid at room temperature so as to facilitate handling and use in the most common electrophotographic processes. Thermal plastics are desirable with melting points significantly above room temperature, but below that of which ordinary paper tends to char so that once the toner images form thereon or transfer to a paper copy sheet, it may be fused in place by subjecting it to heat. This, however, is not a necessary limitation since higher melting resins may be employed and fixed to paper copy sheets by other techniques, such as subjecting the paper copy sheet bearing the powder image to vapors of a solvent for the resin as generally described in U.S. Pat. No. 2,776,907. The resins selected should desirably have good triboelectric properties and have sufficient insulating properties to hold charge so that they may be employed in a number of development systems.

While any suitable transparent resin possessing the properties as above described may be employed in the system of the present invention, particularly good results are obtained with the use of vinyl resins and polymeric esterification products of a dicarboxylic acid and a diol comprising a diphenol. Any suitable vinyl resin may be employed in the toners of the present system including homopolymers or copolymers of two or more vinyl monomers. Typical such vinyl monomeric units include: 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 metchacrylate, butyl methacrylate, and the like; acrylonitri-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 pyrrole, N-vinyl carbazole, N-vinyl indole, N-vinyl pyrrolidene, and the like; and mixtures thereof.

It is generally found that toner resins containing a relatively high percentage of styrene are preferred since greater image definition and density is obtained with their use. The styrene resin employed may be a homopolymer of styrene or styrene homologs or copolymers of styrene with other monomeric groups containing a single methylene group attached to a carbon atom by a double bond. Any of the above typical monomeric units may be copolymerized with styrene by addition polymerization. Styrene resins may also be formed by the polymerization of mixtures of two or more unsaturated monomeric materials with a styrene monomer. 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. However, non-vinyl type thermoplastic resins may also be employed including rosin modified phenol formaldehyde resins, oil modified epoxy resins, polyurethane resins, cellulosic resins, polyether resins, and mixtures thereof.

Polymeric esterification products of a dicarboxylic acid and a diol comprising a diphenol may also be used as a preferred resin material for the toner compositions of the instant invention. The diphenol reactant has the general formula:



wherein R represents substituted and unsubstituted alkylene radicals having from 2 to 12 carbon atoms, alkylidene radicals having from 1 to 12 carbon atoms and cycloalkylidene radicals having from 3 to 12 carbon atoms; R' and R'' represent substituted and unsubstituted alkylene radicals having from 2 to 12 carbon atoms, alkylene arylene radicals having from 8 to 12 carbon atoms and arylene radicals; X and X' represent hydrogen or an alkyl radical having from 1 to 4 carbon atoms; and n_1 and n_2 are each at least 1 and the average sum of n_1 and n_2 is less than 21. Diphenols wherein R represents an alkylidene radical having from 2 to 4 carbon atoms and R' and R'' represent an alkylene radical having from 3 to 4 carbon atoms are preferred because greater blocking resistance, increased definition of xerographic characters and more complete transfer of toner images are achieved. Optimum results are obtained with diols in which R' is a isopropylidene radical and R' and R'' are selected from the group consisting of propylene and butylene radicals because the resins formed from these diols possess higher agglomeration resistance and penetrate extremely rapidly into paper receiving sheets under fusing conditions. Dicarboxylic acids having from 3 to 5 carbon atoms are preferred because the resulting toner resin possesses greater resistance to film formation on reusable imaging surfaces and resist the formation of fines under machine operation conditions. Optimum results are obtained with alpha unsaturated dicarboxylic acids including fumaric acid, maleic acid, or maleic acid anhydride because maximum resistance to physical degradation of the toner as well as rapid melting properties are achieved. Any suitable diphenol which satisfies the above formula may be employed. Typical such diphenols include: 2,2-bis(4-beta hydroxy ethoxy phenyl)-propane, 2,2-bis(4-hydroxy isopropoxy phenyl) propane, 2,2-bis(4-beta hydroxy ethoxy phenyl) pentane, 2,2-bis(4-beta hydroxy ethoxy phenyl)-butane, 2,2-bis(4-hydroxy-propoxy-phenyl)-propane, 2,2-bis(4-hydroxy-propoxy-phenyl)propane, 1,1-bis(4-hydroxy-ethoxy-phenyl)-butane, 1,1-bis (4-hydroxy isopropoxy-phenyl) heptane, 2,2-bis(3-methyl-4-beta-hydroxy ethoxy-phenyl) propane, 1,1-bis(4-beta hydroxy ethoxy phenyl)-cyclohexane, 2,2'-bis(4-beta hydroxy ethoxy phenyl)-norbornane, 2,2'-bis(4-beta hydroxy ethoxy phenyl) norbornane, 2,2-bis(4-beta hydroxy styryl oxyphenyl) propane, the polyoxyethylene ether of isopropylidene diphenol in which both phenolic hydroxyl groups are oxyethylated and the average number of oxyethylene groups per mole is 2.6, the polyoxypropylene ether of 2-butylidene diphenol in which both the phenolic hydroxy groups are oxyalkylated and the average number of oxypropylene groups per mole is 2.5, and the like. Diphenols wherein R represents an alkylidene radical having from 2 to 4 carbon atoms and R' and R'' represent an alkylene radical having from 3 to 4 carbon atoms are preferred because greater blocking resistance, increased definition of xerographic characters and more complete transfer of toner images are achieved. Optimum results are obtained with diols in which R is isopropylidene and R' and R'' are selected from the group consisting of propylene and butylene because the resins formed from these diols possess higher agglomeration resistance and penetrate extremely rapidly into paper receiving sheets under fusing conditions.

Any suitable dicarboxylic acid may be reacted with a diol as described above to form the toner compositions of this invention either substituted or unsubstituted, saturated or unsaturated, having the general formula:

$$HOOC\ R'''_{n_3}\ COOH$$

wherein R''' represents a substituted or unsubstituted alkylene radical having from 1 to 12 carbon atoms, arylene radicals or alkylene arylene radicals having from 10 to 12 carbon atoms and n_3 is less than 2. Typical such dicarboxylic acids including their existing anhydrides are: oxalic acid, malonic acid, succinic acid, glutaric acid, adipic acid, pimelic acid, suberic acid, azelaic acid, sebacic acid, phthalic acid, mesaconic acid, homophthalic acid, isophthalic acid, terephthalic acid, o-phenyleneacetic-beta-propionic acid, itaconic acid, maleic acid, maleic acid anhydride, fumaric acid, phthalic acid anhydride, traumatic acid, citraconic acid, and the like. Dicarboxylic acids having from 3 to 5 carbon atoms are preferred because the resulting toner resins possess greater resistance to film formation on reusable imaging surfaces and resist the formation of fines under machine operation conditions. Optimum results are obtained with alpha unsaturated dicarboxylic acids including fumaric acid, maleic acid, or maleic acid anhydride because maximum resistance to physical degradation of the toner as well as rapid melting properties are achieved. The polymerization esterification products may themselves be copolymerized or blended with one or more other thermoplastic resins preferably aromatic resins, aliphatic resins, or mixtures thereof. Typical thermoplastic resins include: rosin modified phenol formaldehyde resins, oil modified epoxy resins, polyurethane resins, cellulosic resins, vinyl type resins, and mixtures thereof. When the resin component of the toner contains an added resin, the added component should be present in an amount less than about 50 percent by weight based on the total weight of the resin present in the toner. A relatively high percentage of the polymeric diol and dicarboxylic acid condensation product in the resinous component of the toner is preferred because a greater reduction of fusing temperatures is achieved with a given quantity of additive material. Further, sharper images and denser images are obtained when a high percentage of the polymeric diol and dicarboxylic acid condensation product is present in the toner. Any suitable blending technique such as hot melt, solvent, and emulsion techniques may be employed to incorporate the added resin into the toner mixture. The resulting resin blend is substantially homogeneous and highly compatible with pigments and dyes. Where suitable, the colorant may be added prior to, simultaneously with, or subsequent to the blending or polymerization step.

Optimum electrophotographic results are achieved with styrene-butyl methacrylate copolymers, styrene-vinyltoluene copolymers, styrene-acrylate copolymers, polystyrene resins, predominately styrene or polystyrene based resins as generally described in Reissue Pat. No. 25,136 to Carlson, and polystyrene blends as described in Pat. No. 2,788,288 to Rheinfrank and Jones.

Any well-known toner mixing and comminution technique may be employed to provide the toner compositions of the instant invention. For example, the ingredients may be thoroughly mixed by blending and milling and thereafter micropulverized. In addition, spray drying a suspension of the ingredients, a hot melt or a solution of the toner composition may also be employed.

Where carrier materials are employed in connection with the toner compositions of the instant invention in cascade and magnetic brush development, the carrier particles employed may be electrically conductive, insulating, magnetic or nonmagnetic, 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, aluminium potassium chloride, Rochelle salt, sodium nitrate, aluminum nitrate, potassium chlorate, granular zircon, granular silicon, methyl methacrylate, glass, silicon dioxide, flintshot, iron, steel, ferrite, nickel, carborundum, and the like. The carriers may be employed with or without a coating. Many of the foregoing and typical carriers are described by L. E. Walkup in Pat. No. 2,618,551; L. E. Walkup et al, in Pat. No. 2,638,416, and E. N. Wise in Pat. No. 2,618,552. An ultimate coated carrier particle diameter between about 50 microns to about 1,000 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 electrostatic latent images developed by the toner compositions of the instant invention may reside on any surface capable of retaining charge. In electrophotographic applications a photoconductive member is employed to form the electrostatic latent image. The photoconductive layer may comprise an inorganic or an organic photoconductive material. Typical inorganic materials include: sulfur, selenium, zinc sulfide, zinc oxide, zinc cadmium sulfide, zinc magnesium oxide, cadmium selenide, zinc silicate, calcium strontium sulfide, cadmium sulfide, mercuric iodide, mercuric oxide, mercuric sulfide, indium trisulfide, gallium selenide, arsenic disulfide, arsenic trisulfide, arsenic triselenide, antimony trisulfide, cadmium sulfo-selenide, and mixtures thereof. Typical organic photoconductors include: triphenylamine; 2,4-bis(4,4'-diethylamino-phenol)-1,3,4-oxadiazol; N-isopropylcarbazole; triphenylpyrrol; 4,5-diphenylimidazolidinone; 4,5-diphenylimidazolidinethione; 4,5-bis-(4'-amino-phenyl)-imidazolidinone; 1,5-dicyanonaphthalene; 1,4-dicyanonaphthalene; aminophthalodinitrile; nitrophthalodinitrile; 1,2,5,6-tetraazacyclooctatetraene-(2,4,6,8); 2-mercaptobenzothiazole-2-phenyl-4-diphenylidene-oxazolone; 6-hydroxy-2,3-di(pmethoxy-phenyl)-benzofurane; 4-dimethylamino-benzylidene-benzhydrazide; 3-benzylidene-amino-carbazole; polyvinyl carbazole; (2-nitro-benzylidene)-p-bromo-aniline; 2,4-diphenyl-quinazoline; 1,2,4-triazine; 1,5-diphenyl-3-methyl-pyrazoline; 2-(4'-dimethyl-amino phenyl)-benzoxazole; 3-amino-carbazole; polyvinylcarbazole-trinitro-fluorenone charge transfer complex; phthalocyanines, and mixtures thereof.

Any suitable charging technique may be employed in the process of the instant invention. Typical charging methods include charge deposition resulting from air breakdown in the gap commonly referred to as TESI or charging in vacuo with an electron gun.

Any suitable method of exposure may be employed in the process of the instant invention. Typical methods of exposure include: reflex, contact, holographic techniques, nonlens slit scanning systems, and optical projection systems involving lens imaging of opaque-reflection subjects as well as transparent film originals.

Any suitable method of development may be employed in the process of the instant invention. Typical development systems include: cascade development, magnetic brush development, powder cloud development, and liquid development.

Any suitable method of fixing may be employed in the process of the instant invention. Typical methods of fixing include: heat-pressure fusing, radiant fusing, combination radiant, conductive and convention fusing, cold pressure fixing, and flash fusing.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

To further define the specifics of the present invention, the following examples are intended to illustrate and not limit the particulars of the present system. Parts and percentages are by weight unless otherwise indicated.

EXAMPLE I

A 5 percent by weight mixture of CI Disperse Yellow **33** in styrene butylmethacrylate copolymeric resin is prepared in a drum tumbler for 1 hour at about 12 RPM. The material is then poured into a vibra-screw feeder and extruded when machine equilibrium is established. The extruded strands are taken up at the rate of 60 feet per minute and cooled in a water bath at about 120°F followed by forced air drying. Pellets of one-sixteenth to one-eighth inch in diameter are then jetted to about 15 microns average particle size. This toner material is then combined with a methyl terpolymer coated steel bead carrier as described by Jacknow, et al., in Pat. No. 3,627,522 and employed in an electrophotographic imaging machine, a Xerox Model 720 copier. The selenium photoconductor is charged selectively, exposed, and then developed with the yellow developer. After 25,000 prints are obtained, images continue to be produced which possess good contrast, high image density, and desirable appearance. The tribo with the developer continues to maintain a high level.

EXAMPLE II

The process defined in Example I is again performed with the exception that 7 percent of the Disperse Yellow colorant is employed.

EXAMPLE III

The process as outlined in Example I is again repeated with the exception that Disperse Yellow **42** CI **10338** is employed at 6 percent concentration as the colorant.

EXAMPLE IV

The process as outlined in Example I is again performed with the exception that a 4 percent concentration of Disperse Yellow 14 CI 10340 is employed as the colorant.

EXAMPLE V

The procedure as employed in Example I is again performed with the exception that 3 percent of SRA Fast Golden Yellow X11 CI 10336 is employed as the colorant.

EXAMPLE VI

The procedure as outlined in Example I is again performed with the exception that Disperse Orange 15 CI 10350 is employed as the colorant at a concentration of 7 percent.

EXAMPLE VII

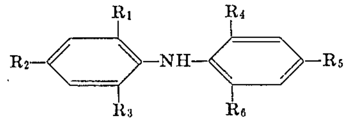
The procedure as outlined in Example I is again performed with the exception that Cellete Brown R CI 10390 is employed as the colorant at a concentration of 6 percent.

Although the present examples were specific in terms of conditions and materials used, any of the above listed typical materials may be substituted when suitable in the above examples with similar results. In addition to the steps used to carry out the process of the present invention, other steps or modifications may be used if desirable. In addition, other materials may be incorporated in the system of the present invention which will enhance, synergize, or otherwise desirably affect the properties of the systems for their present use.

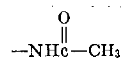
Anyone skilled in the art will have other modifications occur to him based on the teachings of the present invention. These modifications are intended to be encompassed within the scope of this invention.

What is claimed is:

1. An electrostatographic developer composition comprising a carrier, a resin tone and a dye colorant, said dye colorant being substantially dispersed throughout said toner and said dye colorant comprising a compound satisfying the following formula:

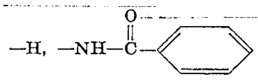


where R_{1-6} = —Cl, —Br, —F, —NO_2,

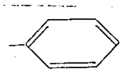


$$-NH\overset{O}{\overset{\|}{C}}-CH_3$$

or other acylamides,



and other aryl carboxamides, $-OCH_3$ and other alkyl or aryl ethers, $-CH_3$ and other alkyl groups,



and other aryl groups both substituted and unsubstituted, —CN, —OH, $-NH_2$, $-NHCH_3$, and other mono and disubstituted alkyl and aryl substituted amines, $-SO_2NH_2$, $-SO_2NH-CH_3$ and other mono and disubstituted alkyl and aryl sulfonamides, —COOH, $-COOCH_3$ and other alkyl and aryl esters.

2. The composition as defined in claim **1** wherein said resin is a member selected from styrenebutyl methacrylate copolymers, styrene-vinyltoluene copolymers, styrene-acrylate copolymers, or poly styrene resins.

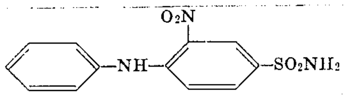
3. The composition as defined in claim **1** wherein said resin is substantially transparent.

4. The composition as defined in claim **1** wherein said resin comprises a polymeric esterification product of a dicarboxylic acid and a diol comprising a diphenol.

5. The composition as defined in claim **1** wherein said resin is a styrene-butyl methacrylate copolymer.

6. The composition as defined in claim **1** wherein said carrier is a methyl terpolymer coated carrier bead.

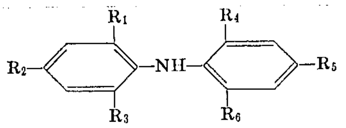
7. An electrostatographic developer composition comprising a carrier, a resin toner and a dye colorant, said dye colorant being substantially dispersed throughout said toner and said colorant comprising a yellow dye satisfying the formula:



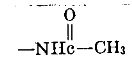
8. The composition as defined in claim **7** wherein said carrier is a methyl terpolymer coated steel bead.

9. The composition as defined in claim **8** wherein said resin is a styrene butyl methacrylate copolymer.

10. An electrostatographic imaging process comprising establishing an electrostatic latent image on a surface and contacting said surface with a powder electrostatographic developer comprising a carrier, a resin toner and a dye colorant, said dye colorant being substantially dispersed throughout said toner and said colorant satisfying the formula:

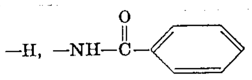


where R_{1-6} = —Cl, —Br, —F, $-NO_2$,



$$-\mathrm{NH}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}-\mathrm{CH_3}$$

or other acylamides,

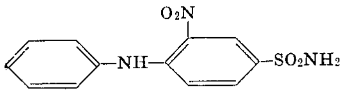


and other aryl carboxamides, $-OCH_3$ and other alkyl or aryl ethers, $-CH_3$ and other alkyl groups,

and other aryl groups both substituted and unsubstituted, —CN, —OH, $-NH_2$, $-NHCH_3$, and other mono and disubstituted alkyl and aryl substituted amines, $-SO_2NH_2$, $-SO_2NH-CH_3$ and other mono and disubstituted alkyl and aryl sulfonamides, —COOH, $-COOCH_3$ and other alkyl and aryl esters.

11. The imaging process as defined in claim **10** further including the steps of transfering said developed image to a receiving surface and fixing said image on said receiving surface.

12. The process as defined in claim **10** wherein said dye colorant satisfies the formula:



13. The process as defined in claim **12** wherein said resin is a styrene butyl methacrylate copolymer and and said carrier is a methyl terpolymer coated steel carrier bead.

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