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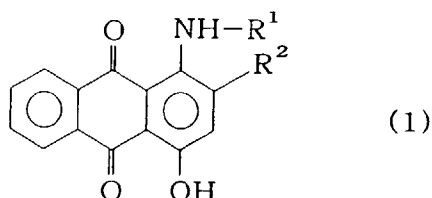
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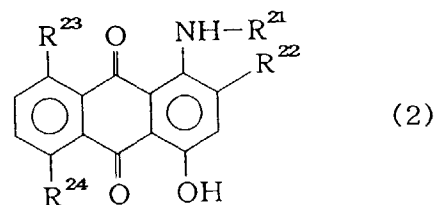
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London WC1R 5LX (GB)**(54) **Dyed toner**

(57) A toner comprising powder particles having a thermoplastic resin as a main component and comprising as colorant a compound of Formula (1):

wherein R¹ is hydrogen or phenyl, and R² is hydrogen,

substituted or unsubstituted alkoxy, substituted or unsubstituted phenoxy, or halogen; or a compound of Formula (2):

wherein R²¹ is hydrogen, alkyl, or substituted phenyl; R²² is hydrogen or halogen; R²³ is hydrogen, hydroxyl, nitro or amino; and R²⁴ is hydrogen, hydroxyl, amino, nitro or alkylamino.**EP 0 872 775 A1**

Description

BACKGROUND OF THE INVENTION

1. Field of the Invention

This invention relates to a toner used in image forming apparatus such as copying machines and printers, and more particularly to a dyed toner comprising powder particles dyed with a colorant.

2. Description of the Related Art

Image forming processes conventionally used in copying machines, printers and facsimile machines are roughly grouped into impact recording and non-impact recording. The non-impact recording includes recording processes such as heat transfer recording, thermal recording, electrophotographic recording, electrostatic recording and ink-jet recording. Of these, in the electrophotographic recording and electrostatic recording, toners are used in order to form images on recording mediums such as paper by development.

The general principle of electrophotography making use of toner will be briefly described here. In this process, first, the surface of a photosensitive member comprising a photoconductive material is electrostatically charged to have a uniform potential. Thereafter, the surface of the photosensitive member is exposed to light in conformity with an image to be outputted, to form an electrostatic latent image. The latent image thus formed is developed at a developing zone by the use of a toner held in an developing assembly, to form a visible image. The visible image formed on the surface of the photosensitive member is transferred to a recording medium such as paper, and then fixed to the recording medium by the action of heat and pressure of a fixing assembly.

Toners used in the electrophotography described above are in the form of fine particles chiefly containing a binder resin component and a colorant component, and are roughly grouped into one-component developers comprised of toner only and two-component developers comprised of a mixture of toner and glass beads or ferrite or iron powder particles.

Such toners are conventionally produced by a pulverization process in which a binder resin and a colorant are melt-kneaded and thereafter the resultant kneaded product is pulverized to have the desired size by means of a pulverizer. However, particles formed by this pulverization contain fine powder in a large quantity, and have had a problem that any excess fine powder must be removed through a classification step for controlling particle size distribution.

Since the fine powder thus removed is collected as useless particles, there has been another problem that the particles obtained as a product are poor in yield with respect to charge weight.

In order to solve the above problems, processes of producing toners by polymerization are proposed, as exemplified by suspension polymerization, emulsion polymerization agglomeration and dispersion polymerization dyeing.

In the process of suspension polymerization, monomers and a colorant are mixed in a bad solvent in which the monomers are insoluble, and the monomers are dispersed therein by means of an agitating blade to produce colored particles.

In this process, although the colored particles can be produced at one-time operation for polymerization, particle diameters of the colored particles are controlled depending on particle diameters of the monomers dispersed in the solvent. Hence, in order to obtain small particle diameters of not larger than 7 μm , it has been necessary to carry out polymerization while controlling heating by stirring. Since, however, there is a limit to the strength of stirring, it has been very difficult to control particle diameter to be 7 μm or smaller.

The particles produced by suspension polymerization also contain fine powder in a large quantity, though not in so large a quantity as those produced by pulverization, and hence have had to be put to a classification step after the colored particles have been dried.

In the process of emulsion polymerization agglomeration, first, in a bad solvent in which monomers are insoluble, the monomers and a polymerization initiator insoluble in the bad solvent are mixed, and the polymerization is initiated at a different site other than dispersed particles of the monomers to form particles of about 1 μm diameter in a large quantity. Thereafter, a solvent in which the particles thus formed and a colorant have been dispersed is treated to cause small particles of about 1 μm diameter to agglomerate to produce small-particle agglomerates of 5 μm or larger diameter.

However, the particle size distribution of the particles produced by this process is affected by stirring when particles agglomerate, and hence has been substantially the same particle size distribution of the particles produced by pulverization.

In the process of dispersion polymerization dyeing, a pulverization initiator is simultaneously dissolved in a good solvent in which monomers are soluble, and polymeric components that have become insoluble with the progress of polymerization are precipitated to form particles.

The particles produced by this process have a narrow particle size distribution and a uniform particle diameter,

but it is difficult for them to be colored simultaneously with polymerization by mixing a colorant at the time of polymerization. Accordingly, it has been necessary to dye the polymer particles with a colorant by again dispersing in a solvent the particles obtained by dispersion polymerization and the colorant.

However, when toners produced by such dispersion polymerization dyeing (hereinafter "dyed toner") are used as recording materials to make color prints, four color dyed toners are used to present full colors, and hence color toners for yellow, magenta, cyan and black colors are required. When, however, full colors are presented using the four color toners, the respective colors must each have a broad range of color reproduction before full colors can be faithfully reproduced.

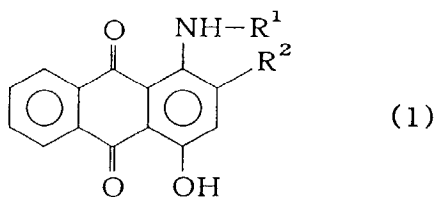
Polymer particles can be dyed by causing dyes to move into polymer particles. However, in almost all instances, dyes stand only a little moved into colored particles after they have been dyed, even when a dye solution used when they are dyed have a sufficient concentration. Thus, there has been a problem that particles having been dyed stand dyed in a low density.

There also has been a problem that some types of dyes have a poor light-fastness and are inferior in respect of sublimation properties for which resin films are superposed to examine color migration.

SUMMARY OF THE INVENTION

The present invention was made in order to solve the above problems. Accordingly, an object of the present invention is to provide a red-color dyed toner or blue-color dyed toner having a narrow particle size distribution, having superior light-fastness and sublimation properties and being dyed in a high density.

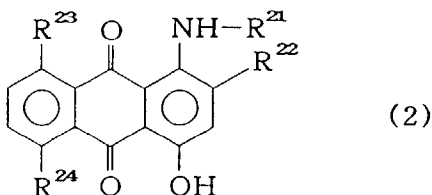
To achieve this object, the red-color dyed toner of the present invention comprises powder particles having a thermoplastic resin as a main component and being dyed with a colorant, wherein the colorant comprises a compound represented by the following Formula (1):



wherein R¹ represents a hydrogen atom or a phenyl group; R² represents a hydrogen atom, a substituted or unsubstituted alkoxy group, a substituted or unsubstituted phenoxy group or a halogen atom.

The red-color dyed toner of the present invention constituted as described above comprises powder particles having a thermoplastic resin as a main component and being dyed with a colorant, and the colorant is the compound represented by the above Formula (1). Thus, it has a narrow particle size distribution, has superior light-fastness and sublimation properties and can be dyed in red in a high density.

The blue-color dyed toner of the present invention comprises powder particles having a thermoplastic resin as a main component and being dyed with a colorant, wherein the colorant comprises a compound represented by the following Formula (2):



wherein R²¹ represents a hydrogen atom, an alkyl group or a substituted phenyl group; R²² represents a hydrogen atom or a halogen atom; R²³ represents a hydrogen atom, a hydroxyl group, a nitro group or an amino group; and R²⁴ represents a hydrogen atom, a hydroxyl group, an amino group, a nitro group or an alkylamino group.

The blue-color dyed toner of the present invention constituted as described above comprises powder particles having a thermoplastic resin as a main component and being dyed with a colorant, and the colorant is the compound represented by the above Formula (2). Thus, it has a narrow particle size distribution, has superior light-fastness and

sublimation properties and can be dyed in blue in a high density.

This and other objects, features and advantages of the present invention are described in or will become apparent from the following detailed description of the invention.

5 DETAILED DESCRIPTION OF THE INVENTION

The red-color or blue-color dyed toner of the present invention is constituted chiefly of thermoplastic resin particles dyed with a specific colorant.

10 The thermoplastic resin particles used in the present invention may be any of those obtained by pulverization, suspension polymerization or emulsion polymerization agglomeration. In order to obtain particles with a narrow particle size distribution, it is desirable to use a process such as seed polymerization or dispersion polymerization. The dispersion polymerization is also called precipitation polymerization, in which a polymerization initiator and a polymeric dispersing agent are simultaneously dissolved in an organic solvent in which polymerizable monomers have been dissolved, and polymerization is initiated while maintaining a constant temperature. A surface-active agent and a cross-
15 linking agent may also optionally be added.

Materials used in such dispersion polymerization dyeing will be described below while giving their examples.

Organic solvent:

20 The organic solvent in which the polymerizable monomers used in the present invention may include, e.g., alcohols such as methanol, ethanol, isopropyl alcohol, n-butanol, s-butanol, t-butanol, n-amyl alcohol, s-amyl alcohol, t-amyl alcohol, isoamyl alcohol, isobutyl alcohol, isopropyl alcohol, 2-ethylbutanol, 2-ethylhexanol, 2-octanol, n-octanol, n-decanol, cyclohexanol, n-hexanol, 2-heptanol, 3-heptanol, 3-pentanol, methylcyclohexanol, 2-methyl-2-butanol, 3-methyl-2-butanol, 3-methyl-1-butyn-3-ol, 4-methyl-2-pentanol and 3-methyl-1-pentyn-3-ol, any of which may be used
25 alone or in the form of a mixture of two or more.

An additional organic solvent may also be used in combination with any of these alcohols. Such an additionally usable organic solvent may include, e.g., hydrocarbon type solvents such as hexane, toluene, cyclohexane, benzene and xylene; ethers such as ethyl benzyl ether, dibutyl ether, dipropyl ether, dibenzyl ether, dimethyl ether, tetrahydrofuran, methyl vinyl ether and ethyl vinyl ether; ketones such as acetaldehyde, acetone, acetophenone, diisobutyl ketone, diisopropyl ketone and cyclohexanone; and esters such as ethyl formate, ethyl acetate, methyl acetate, ethyl
30 stearate, methyl salicylate. Water may also be used. These solvents are used for adjustment of the SP value of the alcohol.

It is suitable for the organic solvent to be used in a weigh ratio to monomers of from 100:5 to 100:80.

35 Monomers:

As a monomer having a polymerizable functional group, a compound containing a vinyl group may be used, including, e.g., styrene monomers such as styrene, methylstyrene, ethylstyrene, 2,4-dimethylstyrene, p-n-butylstyrene and p-t-butylstyrene; methyl fatty acid monocarboxylic esters such as methyl acrylate, ethyl acrylate, n-butyl acrylate,
40 2-ethylhexyl acrylate, cyclohexyl acrylate, methyl methacrylate, ethyl methacrylate, n-butyl methacrylate, 2-ethylhexyl methacrylate, stearyl methacrylate and lauryl methacrylate; vinyl ethers such as methyl vinyl ether, ethyl vinyl ether, n-propyl vinyl ether and n-butyl vinyl ether; and vinyl compounds such as acrylonitrile, methacrylonitrile, vinyl acetate, vinyl chloride, ethylene, propylene and chloroprene; any of which may be used alone or in the form of a mixture of two or more.

45 Polymerization initiator:

The polymerization initiator for polymerizing the above monomer(s) may preferably be added in an amount of from 0.001 to 10% by weight, and may include, e.g., lauryl peroxide, benzoyl peroxide and azobisisobutyronitrile.

50 Dispersing agent:

The dispersing agent is mixed in the organic solvent from the beginning of polymerization so that polymer particles formed can be prevented from agglomerating, at the same time the polymerization proceeds and particles begin to be
55 formed. It may be mixed in an amount of from 0.1 to 30 parts by weight based on 100 parts by weight of the mixture of the organic solvent and monomers. This dispersing agent may include, e.g., polystyrene, polyvinyl acetate, polymethyl methacrylate, polydimethylsiloxane, polyvinyl chloride, polyethylene, polypropylene, polylauryl methacrylate, polyoxyethylene, polyvinyl alcohol, polyacrylic acid, polymethacrylic acid, polyacrylamide, polyvinyl pyrrolidone, polyeth-

yleneimine, polyvinyl methyl ether, poly-4-vinyl pyridine and polystyrene sulfone.

In the organic solvent as described above, the monomer and the dispersing agent are appropriately mixed at a normal temperature, and the obtained mixture is purged with nitrogen. Thereafter, the polymerization initiator is introduced thereto to obtain a dispersion, and the temperature of the dispersion is raised to initiate polymerization. Upon the polymerization, at the time the temperature has reached 30 to 40 °C, the dispersion begins to become turbid, where polymeric components that can not dissolve in the solvent can be seen to begin to be precipitated. The polymerization is continued within the range of 50 to 100 °C, provided that the polymerization temperature should be decided in view of a boiling point of the solvent, a decomposition rate of the polymerization initiator and the like.

The temperature of the dispersion is kept constant with continuous stirring until the polymerization is completed, which are done for 5 to 24 hours while making sure of particle size distribution and conversion. After the polymerization is completed, the resultant polymer particle dispersion having been kept at a constant temperature is cooled to normal temperature, thus a series of polymerization operations are completed. The polymer particle dispersion is set on a centrifugal separator to separate particles from the liquid phase. The particles obtained are again dispersed in a solvent in order to wash away unreacted monomers or the dispersing agent which have adhered to the particle surfaces. The washing is repeated, and, at the stage where any residues are seen to be no longer present on the particle surfaces, the thermoplastic resin particles obtained are dried.

After about one hour from the beginning of the polymerization, the formation of the polymer particles can be confirmed, and the particles have a particle average size of 0.1 to 1 µm. In the case of a dispersion polymerization, polymerization is generally continued until a conversion rate of from a monomer to a polymer reaches 90 to 95%, although a conversion rate does not reach 100%. The conversion rate rapidly increases at the initial stage of polymerization, but gradually increases at the last stage thereof. The polymerization is stopped at the time when the particle size reaches the intended size.

In the case of synthesizing the particles according to dispersion polymerization, the particle size can be adjusted within the range of 1 to 50 µm. A preferable average particle size of a dry toner is 5 to 15 µm.

In conventional toner manufacture processes such as suspension polymerization or pulverization, toner size can be adjusted within the range of 5 to 15 µm, but a dispersion degree (rate of a volume-based particle size to a particle-number-based particle size) is 1.3 to 1.5. On the other hand, in dispersion polymerization, particles having a dispersion degree of 1.2 or less can be manufactured.

A molecular weight of particles obtained according to dispersion polymerization can be adjusted by varying the concentration of an initiator, a dispersing agent or a monomer. A molecular weight distribution can be varied by selecting a chain transfer agent or a monomer to be used. A linking agent can be used upon dispersion polymerization. By adjusting the molecular weight, a molecular weight distribution, thermal properties and a shelf stability of the toners can be changed.

In order to fix the toners on a recording medium by heat and pressure, the particles constituting the toners are required to have a molecular weight of 100,000 or less, a linking degree of 50% or less, an appropriate softening point as a thermoplastics, and a flow-starting temperature of 200°C or less when measured by a flow tester under a pressure of 10kg/cm² and a heat-up rate of 1°C/min.

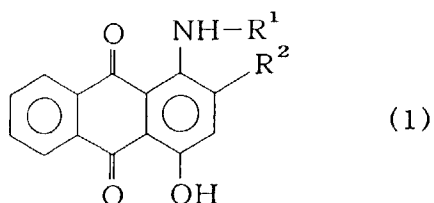
The softening temperature of the particles affects a shelf stability of the toners. If the softening point is too low, blocking of the toners is caused upon storage, whereby the toners are poor in toner-characteristics.

The softening point is preferably 50 °C or more in order to have a good shelf stability in the environment. The softening point can be changed depending on the composition of monomers used, and affects thermal properties of the particles. Accordingly, the softening point of the particles is preferably about 90 °C or less.

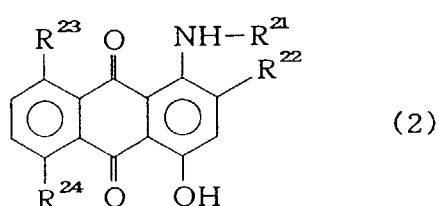
The thermoplastic resin particles thus synthesized are again dispersed in a solvent for dyeing, containing a colorant. The solvent used for dyeing is conditioned on not dissolving the thermoplastic resin particles. It may include, e.g., alcohols such as methanol, ethanol, isopropyl alcohol, n-butanol, s-butanol, t-butanol, n-amyl alcohol, s-amyl alcohol, t-amyl alcohol, isoamyl alcohol, isobutyl alcohol, isopropyl alcohol, 2-ethylbutanol, 2-ethylhexanol, 2-octanol, n-octanol, n-decanol, cyclohexanol, n-hexanol, 2-heptanol, 3-heptanol, 3-pentanol, methylcyclohexanol, 2-methyl-2-butanol, 3-methyl-2-butanol, 3-methyl-1-butyn-3-ol, 4-methyl-2-pentanol and 3-methyl-1-pentyn-3-ol, any of which may be used alone or in the form of a mixture of two or more.

The thermoplastic resin particles may preferably be mixed in an amount of from 1 to 50 parts by weight, and the colorant in an amount of from 1 to 30 parts by weight, based on 100 parts by weight of the above organic solvent.

The colorant used in the present invention is a dye represented by the following Formula (1) for the red-color dyed toner, or a dye represented by the following Formula (2) for the blue-color dyed toner:



10 wherein R¹ represents a hydrogen atom or a phenyl group; R² represents a hydrogen atom, a substituted or unsubstituted alkoxy group such as alkoxyalkoxy, alkoxyalkoxyalkoxy, hydroxyalkoxy, a substituted or unsubstituted phenoxy group such as alkylphenyl(e.g., methylphenoxy), alkoxyalkylaminosulfonylphenoxy(e.g., 3-ethoxypropylaminosulfonylphenoxy), a halogen atom such as Br.

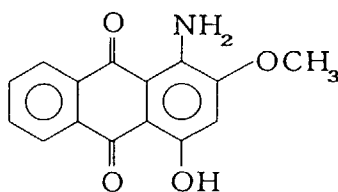


25 wherein R²¹ represents a hydrogen atom, an alkyl group such as methyl or a substituted phenyl group such as p-methylphenyl; R²² represents a hydrogen atom or a halogen atom such as Br; R²³ represents a hydrogen atom, a hydroxyl group, a nitro group or an amino group; and R²⁴ represents a hydrogen atom, a hydroxyl group, an amino group, a nitro group or an alkylamino group such as methylamino.

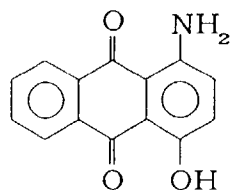
30 The above dye used as the colorant in the present invention may include, as red-color dyes, C.I. Disperse Red 4, 15, 53, 55, 114, 59, 60, 71, 83, 91 and 92, and C.I. Disperse Violet 23, 27, 30, 37 and 17; and as blue-color dyes, C.I. Disperse Blue 72, 81, 26, 27, 71, 56 and 59, C.I. Solvent Blue 90 and C.I. Solvent Violet 13.

Some of these dyes and those used in Examples and Comparative Examples described later are shown below with their structural formulas.

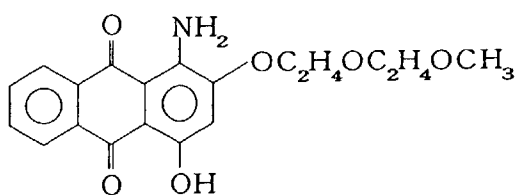
C.I. Disperse Red 4



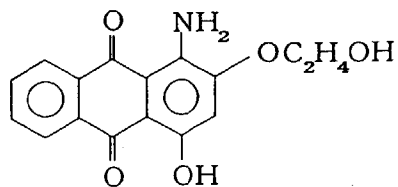
C.I. Disperse Red 15



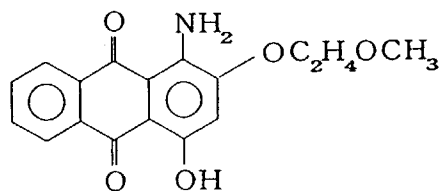
C.I. Disperse Red 53



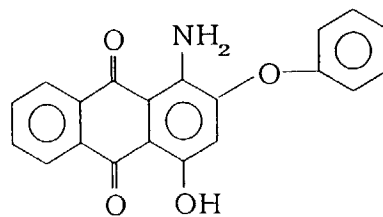
C.I. Disperse Red 55



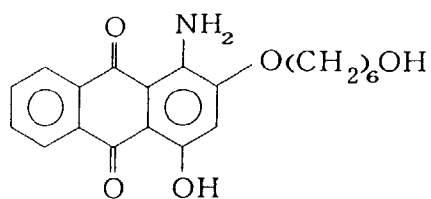
C.I. Disperse Red 59



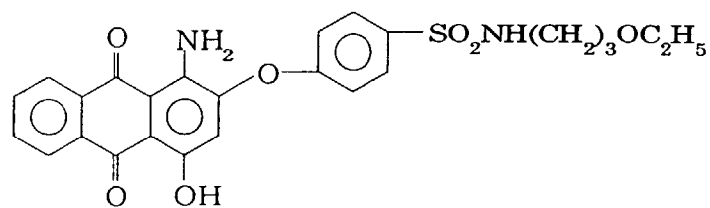
C.I. Disperse Red 60



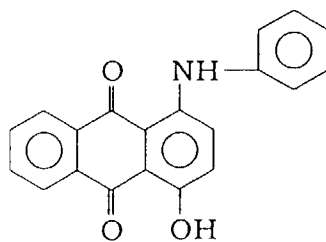
C.I. Disperse Red 91



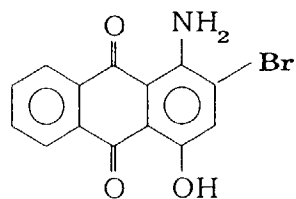
C.I. Disperse Red 92



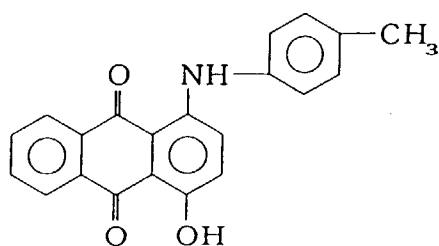
C.I. Disperse Violet 23



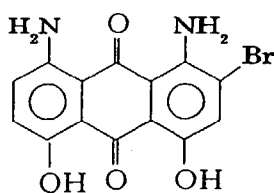
C.I. Disperse Violet 17



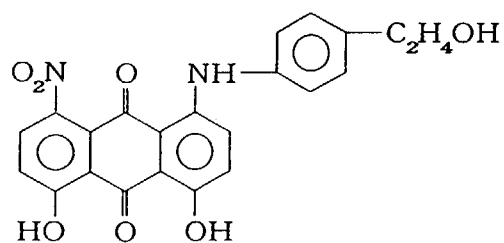
C.I. Disperse Blue 72



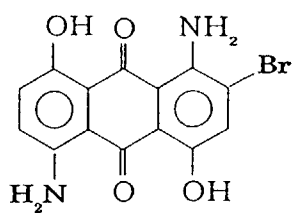
C.I. Disperse Blue 81



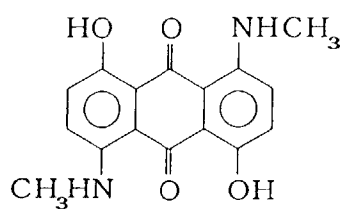
C.I. Disperse Blue 27



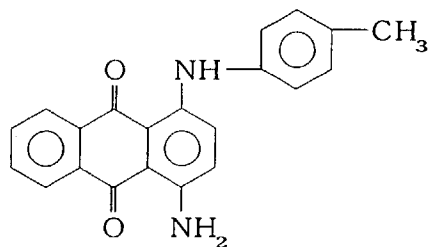
C.I. Disperse Blue 56



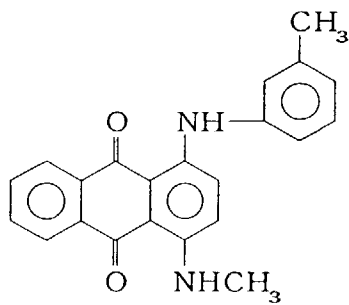
C.I. Disperse Blue 26



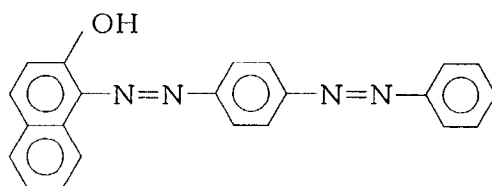
C.I. Solvent Blue 11



C.I. Solvent Blue 63



C.I. Solvent Red 23



The dispersion in which the thermoplastic resin particles and colorant have been dispersed is heated to 30 to 40 °C at which the temperature is kept constant, and the particles are dyed while stirring the dispersion over a period of from 30 minutes to 5 hours. After the dyeing is completed, the temperature is dropped to normal temperature, and colored particles and solvent are separated by means of a centrifugal separator. Washing with solvent and separation are further repeated in order to wash away any residual colorant adhering to the surfaces of the colored particles. Masses of the colored particles separated from the solvent are dried with a stirring dryer kept at 30 to 40 °C, in order to remove the solvent adsorbed on the particles.

The particles are dyed in an organic solvent which should be so selected as not to solve the particles. The particles dispersed in the solvent preferably swell therein. The heated, swelling particles adsorb dyes. The higher the heating temperature, the faster the dyeing velocity and the higher the dye concentration in the particles, but this causes the particles to weld together, and the toner constituted of the welded particles loses appropriate functions as a toner. Accordingly the particles are dyed preferably at a temperature of the glass transition point or less of the particles.

The particles are considered to be dyed in the depth of several μm from the surface thereof. Accordingly, if the particles have a diameter of several μm , they are considered to be dyed up to the central portion thereof, where it is considered that the dye permeates into the inside of the particles, and accordingly that the dye preferably has a chemical structure having a good affinity for the composition of the particles. Of dispersion dyes and oil-soluble dyes, the dye represented by the formula (1) or (2) can dye the particles very well.

As dyes other than the dyes used in the present invention, there are, for example, acidic dyes, basic dyes and reaction dyes. These dyes dye the particles by forming bonds between themselves and the functional groups of the particles.

In order to attain satisfactory durability (running performance) and fixing performance, fine particles or a release agent may be implanted into the thermoplastic resin particles thus dyed, using a machine such as Hybridizer or Mech-anofusion.

EXAMPLE

The dyed toner of the present invention will be described below in greater detail by giving examples.

Polymer particle Production 1

In a four-necked flask provided with an agitating blade, a condenser, a thermometer and a gas feed pipe, 50 parts by weight of methanol and 150 parts by weight of isopropyl alcohol were mixed, and 20 parts by weight of polyvinyl pyrrolidone (K-30) was further dissolved therein. To the resultant solution, 150 parts by weight of styrene, 40 parts by weight of n-butyl acrylate and 8 parts by weight of 2,2-azobisisobutyronitrile were added and stirred to form a transparent solution. With stirring, the inside of the flask was purged with nitrogen gas, and the temperature was raised to 60 °C to initiate polymerization while rotating the agitating blade at 100 r.p.m. On lapse of 10 minutes after heating was started, the solution began to become turbid, in the state of which polymerization was carried out for 10 hours. After 7 hours from the initiation of polymerization, the temperature was restored to normal temperature while dropwise adding 200 parts by weight of a 1:1 mixed solvent of water and methanol, thus the polymerization was completed to obtain a slurry.

The slurry thus obtained was first-time centrifuged using a filter of 3 μm in pore size. After the resultant filtrate was re-dispersed in the mixed solvent of water and methanol, the mixture was second-time centrifuged using a filter of 3 μm in pore size, followed by drying for 24 hours to obtain thermoplastic resin particles, which had a volume-average particle diameter D_v of 7.2 μm and a ratio (degree of dispersion) of volume-average particle diameter D_v to number-

average particle diameter D_p , D_v/D_p , of 1.07.

Polymer particle Production 2

The procedure of Polymer particle Production 1 was repeated under the same formulation except that the composition of monomers was replaced with 150 parts by weight of styrene and 40 parts by weight of ethyl acrylate. Thermoplastic resin particles thus obtained had a volume average particle diameter D_v of 7.11 μm and a D_v/D_p of 1.12.

Example 1

Into a 300 ml beaker, 100 parts by weight of methanol was poured, and 3 parts by weight of C.I. Disperse Red 4 was added, and these were dissolved in a 40°C water bath with stirring, where 30 parts by weight of the thermoplastic resin particles obtained in Polymer particle Production 1 were dispersed therein. The resultant dispersion was stirred for 1 hour under reflux with heating to carry out dyeing, which was then first-time centrifuged using a filter of 3 μm in pore size. The resultant filtrate was re-dispersed in a 1:1 mixed solvent of water and methanol, and the mixture obtained was second-time centrifuged using a filter of 3 μm in pore size. The particles thus obtained were dried for 24 hours to obtain red dyed particles.

In 100 parts by weight of the particles, 3 parts by weight of hydrophobic silica (RA200H) was mixed, followed by agitation with a mixer to form a positively chargeable dyed toner. Its charge quantity was +32 $\mu\text{C/g}$ as measured with a blow-off charge quantity measuring device using a mixture prepared by mixing 4 parts by weight of the dyed toner in 100 parts by weight of iron powder.

This dyed toner was loaded in a developing process unit in which apertures are provided and a voltage applied to electrodes arranged for all apertures is controlled to control the flying of toner, and images were printed. As a result, red images were obtainable without causing offset even during heat fixing, giving a sufficient image density of 1.51 as reflection density.

The reflection density was measured with Macbeth Densitometer RD-917. When red images free of unevenness are intended, it is desirable for the reflection density to be controlled at 1.4 or above.

Example 2

Into a 300 ml beaker, 100 parts by weight of methanol was poured, and 3 parts by weight of C.I. Disperse Blue 27 was added, and these were dissolved in a 40 °C water bath with stirring, where 30 parts by weight of the thermoplastic resin particles obtained in Polymer particle Production 1 were dispersed therein. The resultant dispersion was stirred for 1 hour under reflux with heating to carry out dyeing, which was then first-time centrifuged using a filter of 3 μm in pore size. The resultant filtrate was re-dispersed in a 1:1 mixed solvent of water and methanol, and the mixture obtained was second-time centrifuged using a filter of 3 μm in pore size. The particles thus obtained were dried for 24 hours to obtain blue dyed particles.

In 100 parts by weight of the particles, 3 parts by weight of hydrophobic silica (RA200H) was mixed, followed by agitation with a mixer to form a positively chargeable dyed toner. Its charge quantity was +32 $\mu\text{C/g}$ as measured with a blow-off charge quantity measuring device using a mixture prepared by mixing 4 parts by weight of the dyed toner in 100 parts by weight of iron powder.

This dyed toner was loaded in a developing process unit in which apertures are provided and a voltage applied to electrodes arranged for all apertures is controlled to control the flying of toner, and images were printed. As a result, blue images were obtainable without causing offset even during heat fixing, giving a sufficient image density of 1.42 as reflection density.

The reflection density was measured with Macbeth Densitometer RD-917. When blue images free of unevenness are intended, it is desirable for the reflection density to be controlled at 1.4 or above.

Examples 3 to 7, Comparative Examples 1 to 3

Dyed toners of Examples 3 to 7 and Comparative Examples 1 to 3 were produced in the same manner as in Examples 1 and 2 using the same solvents and in the same material quantities, but using dyes and thermoplastic resin particles as shown in Table 1. The charge quantity and image density were also measured in the same way.

Results obtained are shown together in Table 1.

Table 1

	Dye Used	Thermoplastic Fine particle	Color/Charge/OD* ($\mu\text{C/g}$)
Example:			
1	C.I. Disperse Red 4	Polymer particle Production 1	Red/ +32/1.51
2	C.I. Disperse Red 15	Polymer particle Production 2	Red/ +25/1.42
3	C.I. Disperse Blue 27	Polymer particle Production 1	Blue/ +30/1.70
4	C.I. Disperse Red 53	Polymer particle Production 1	Red/ +41/1.46
5	C.I. Disperse Blue 2	Polymer particle Production 2	Blue/ +35/1.55
6	C.I. Disperse Blue 56	Polymer particle Production 1	Blue/ +34/1.46
7	C.I. Disperse Blue 72	Polymer particle Production 1	Blue/ +28/1.44
Comparative Example:			
1	C.I. Solvent Blue 63	Polymer particle Production 1	Blue/ +22/1.02
2	C.I. Solvent Blue 11	Polymer particle Production 1	Blue/ +23/0.98
3	C.I. Solvent Red 23	Polymer particle Production 1	Red/ +22/1.21

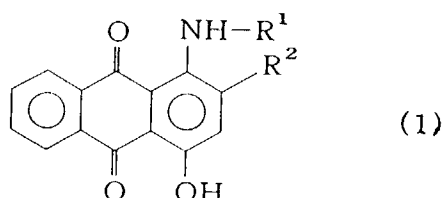
OD*: Optical density of images prepared by using the toner

As is clear from the foregoing results, since the red-color dyed toners of Examples 1, 2 and 4 made use of the compound of Formula (1) as the colorant, they showed a narrow particle size distribution, showed superior light-fastness and sublimation properties and were dyed in red in a high density. Also, since the blue-color dyed toners of Examples 3 and 5 to 7 made use of the compound of Formula (2) as the colorant, they showed a narrow particle size distribution, showed superior light-fastness and sublimation properties and were dyed in blue in a high density.

The entire disclosure of the specification, claims and summary of Japanese Patent application No. 9-98647 filed on April 16, 1997 is herein incorporated by reference in its entirety.

Claims

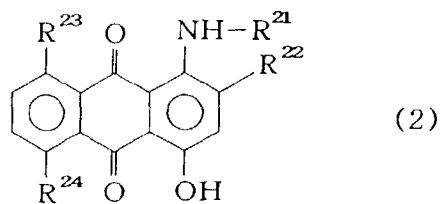
1. A toner comprising powder particles having a thermoplastic resin as a main component and comprising as colorant a compound of Formula (1):



wherein R¹ is hydrogen or phenyl, and R² is hydrogen, substituted or unsubstituted alkoxy, substituted or unsubstituted phenoxy, or halogen.

2. A toner according to claim 1, wherein R¹ is hydrogen.
3. A toner according to claim 1 or claim 2, wherein R² is methoxy.
4. A toner according to claim 1 or claim 2, wherein R² is selected from a 2-(2'-methoxyethoxy)ethoxy, 2-hydroxyethoxy, 2-methoxyethoxy and 6-hydroxyhexyloxy.
5. A toner according to claim 1 or claim 2, wherein R² is selected from p-(3-ethoxy)propylaminosulfonyl)phenoxy, unsubstituted phenoxy and p-(3-ethoxypropylaminosulfonyl)phenoxy.
6. A toner according to claim 1 or claim 2, wherein R² is bromine.
7. A toner according to claim 1, wherein R¹ is phenyl and R² is hydrogen.

8. A toner comprising powder particles having a thermoplastic resin as a main component and comprising as colorant a compound of Formula (2):



wherein R²¹ is hydrogen, alkyl, or substituted phenyl; R²² is hydrogen or halogen; R²³ is hydrogen, hydroxyl, nitro or amino; and R²⁴ is hydrogen, hydroxyl, amino, nitro or alkylamino.

- 15
9. A toner according to claim 8, wherein R²¹ is hydroxyalkylphenyl, R²³ is nitro and R²⁴ is hydroxyl.
10. A toner according to claim 9, wherein R²¹ is hydroxyethylphenyl.
- 20
11. A toner according to claim 8, wherein R²¹ is alkyl, R²³ is hydroxyl and R²⁴ is alkylamino.
12. A toner according to claim 11, wherein R²¹ is methyl and R²⁴ is methylamino.
- 25
13. A toner according to claim 8, wherein R²¹ is hydrogen, R²² is halogen, R²³ is hydroxyl and R²⁴ is amino.
14. A toner according to claim 8, wherein R²¹ is alkylphenyl, and R²³ and R²⁴ are hydrogen.
15. A toner according to claim 14, wherein R²¹ is p-methylphenyl.
- 30
16. A toner according to claim 8, wherein R²¹ is hydrogen, R²² is halogen, R²³ is amino and R²⁴ is hydroxyl.
17. A toner according to claim 13 or claim 16, wherein R²² is bromine.
- 35
18. Use of a toner according to any preceding claim in formation of an image.



European Patent
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EUROPEAN SEARCH REPORT

Application Number
EP 98 30 2957

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
X	DE 26 44 850 A (SUBLISTATIC) 14 April 1977 * page 17, paragraph 2; claim 1; example 2 * * page 17, line 17 - line 19 * * page 19, paragraph 1 * ---	1-5,8,18	G03G9/09
X	EP 0 330 487 A (MITSUI TOATSU) 30 August 1989 * page 3, line 61 - line 63; claim 1; examples 1-3,5,6,8 * * page 9, line 59 - page 10, line 10 * ---	1-3,5,14,18	
X	DATABASE WPI Section Ch, Week 9620 Derwent Publications Ltd., London, GB; Class A05, AN 96-197809 XP002072158 & JP 08 069 128 A (MINOLTA), 12 March 1996 * abstract * ---	1,2,5,18	
X	PATENT ABSTRACTS OF JAPAN vol. 14, no. 402 (P-1099), 30 August 1990 & JP 02 154276 A (MITSUBISHI), 13 June 1990, * abstract * ---	1,2,6,18	TECHNICAL FIELDS SEARCHED (Int.Cl.6) G03G
X	DE 20 25 503 A (XEROX) 3 December 1970 * claim 1; example 1 * ---	1,2,8,18	
A	PATENT ABSTRACTS OF JAPAN vol. 13, no. 570 (P-977), 18 December 1989 & JP 01 237667 A (MITSUI TOATSU), 22 September 1989, * abstract * -----	8-17	
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 21 July 1998	Examiner Vanhecke, H
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document	

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