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(54) DRY DEVELOPMENT USING AN ENCAPSULATED TONER

(71) We, CANON KABUSHIKI KAISHA, a Japanese Company of 30-2 Shimomaru-ko 3-chome, Ohta-Ku, Tokyo, Japan do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:-

5 *BACKGROUND OF THE INVENTION* 5

It is well known in the prior art to develop electrostatic latent images contained on a dielectric or electrophotographic surface by attraction thereto of electroscopic marking particles which may be applied by the cascade, magnetic or powder cloud developing methods.

10 The production of electroscopic marking particles for use in each of such developing processes has been in the past a complicated and lengthy procedure in that such developing methods require the production of finely ground dry particles of carefully controlled particle size and triboelectric properties.

15 Each of the prior art developing methods described also can give rise to atmospheric pollution problems in that they can cause the generation of harmful atmospheric dust or vapors.

The electroscopic marking particles are normally referred to as toners, and accordingly in the following disclosure of the present invention the actual electroscopic marking particles will be referred to as a toner.

20 *DESCRIPTION OF THE INVENTION* 20

According to the present invention there is provided electroscopic marking particles for the dry development of electrostatic latent images which particles comprise an inner aqueous phase encapsulated in an outer shell of hydrophobic silica, the aqueous phase containing a water soluble dye or a water dispersible pigment.

25 The toners of the present invention contain water and thus cause less atmospheric pollution and can be prepared by a simple method which readily enables the particle size to be readily controlled. Thus, they may be prepared by first forming a solution or saturated solution or super saturated solution or suspension of dye or pigment in an aqueous medium, adding a small but finite quantity of hydrophobic silica to the thus formed aqueous solution or suspension, and subjecting the mixture to high shear in, for example, a Waring blender. Individual droplets of water containing the dye or pigment are formed and immediately become coated with a layer of hydrophobic silica. The hydrophobic silica prevents re-agglomeration of the aqueous phase and the resultant product is essentially a free flowing powder of particle size governed by viscosity, blending efficiency and component proportions. Preferably the toner particles are such that they include from 50 to 200 parts by weight of said aqueous phase per 100 parts by weight of hydrophobic silica.

35 The thus formed toner particles have been found to be surprisingly robust and to possess flow properties adequate for the developing of electrostatic latent images contained on the surface of a dielectric or photoconductive recording member without necessarily requiring admixture of carrier particles such as those used in cascade and magnetic brush developing methods. However they may be incorporated as toner material for use with the prior art developing methods if so desired.

40 The toned image deposit formed on the recording member surface may advantageously be transferred to a receiving member surface such as a plain paper surface by prior art electrostatic methods or by simple pressure contact. The receiving member such as a bond 45

paper sheet is brought into contact with the toned image deposit on the recording member surface in the nip of a pair of pressure rollers. The applied pressure is sufficient to displace the hydrophobic silica layer on the water droplets, thus allowing the aqueous phase to contact the receiving member surface. The dye or pigment contained in the aqueous phase is adsorbed or absorbed by the receiving member surface as it becomes wetted by the aqueous phase of the toner particles. The surface of the photoconductive or dielectric recording member is generally water repellent and consequently residual toner deposits are easily removed therefrom, allowing re-use of the recording member if desired. Alternatively the dielectric or photoconductive recording member containing the image deposit thereon can itself be passed through the nip of a pair of pressure rollers to allow the aqueous phase to contact the recording member surface, and in those instances where such recording member surface is prepared to be hydrophilic the dye or pigment contained in said aqueous phase will be adsorbed or absorbed by such surface to form a fixed image thereon. In this case it is preferable that the surface of the pressure roller contacting the surface of the recording member should be less water adsorbing or absorbing than the surface of the recording member.

Examples of suitable water soluble dyes are crystal violet, methylene blue, naphthalene black, disulphine blue, rose bengal, eosin Y, and sodium fluorescein, which may be included within the water in fully or partially dissolved form. Suitable water dispersible pigments are, for example, those which are normally supplied as approximately 50% pigment solids dispersions in a glycol/water mixture. Examples of such pigments are C.I. Pigment Black 6 (C.I. 77266), C.I. Pigment Blue 15 (C.I. 74160), C.I. Pigment Red 3 (C.I. 12120) and C.I. Pigment Yellow 1 (C.I. 11680). For use in accordance with the present invention such aqueous pigment dispersion may be diluted with further water as desired to allow the production transferred or directly developed image deposits of the desired colour intensity. The toner may include, in its aqueous phase, water dispersible magnetic particles, such as pigment grade magnetite or ferrite particles. In this case the toner can be applied by means of a magnetic applicator without requiring the admixing of magnetic carrier particles.

The hydrophobic silica used to form the outer or barrier layer around the individual water droplets is preferably of very small particle size, such as about 7 millimicron average diameter in order that toner particle droplets of small mean diameter may be produced as a free flowing apparently dry powder. Such hydrophobic silica particles normally contain a silicone surface layer, generally of the trimethylsiloxy type.

If desired the aqueous phase may also contain water soluble or water dispersible image fixing materials whereby on rupturing of the encased water droplets (by means of, for example, a pressure roller) the contents thereof contact and adhere to the recording member surface to produce a fixed image deposit on the recording member surface. Examples of suitable image-fixing materials include glycerine, glucose, sucrose, polyvinyl alcohol, propionic acid, polyethylene glycol, ethylene glycol, barium propionate, water soluble electroconductive resins of the quaternary ammonium type, lactose, fructose, maleic anhydride and succinimide.

We have also found that, in those instances where a water soluble dye is used, small quantities of hydrophilic filler material may be included within the aqueous phase to further control droplet size and consequently to control image definition, deformation and spread in transfer. Such filler material may be, for example, alumina hydrate or magnesium oxide.

In accordance with an embodiment of the invention, the toner may be prepared by dissolving the water soluble dye in water, and admixing the resultant solution with hydrophobic silica particles in a high shear blender to obtain the desired particles in the form of an inner aqueous phase containing said water soluble dye and encapsulated in an outer shell formed of said hydrophobic silica particles.

In another embodiment, the toner may be prepared by dissolving the water soluble dye and a water soluble image-fixing material in water, dispersing a water dispersible pigment in the resultant solution and admixing hydrophobic silica particles with the resultant dispersion in a high shear blender to obtain the desired particles in the form of an inner aqueous phase containing said water soluble dye, said water soluble image-fixing material and said pigment, and encapsulated in an outer shell formed of said hydrophobic silica particles.

In a further embodiment, the toner may be prepared by dissolving a water soluble image-fixing material in water, dispersing in the resultant solution the water dispersible pigment, and admixing the resultant dispersion with hydrophobic silica particles in a high shear blender to obtain the desired particles in the form of an inner aqueous phase containing said water soluble image-fixing material and said pigment and encapsulated in an outer shell formed of said hydrophobic silica particles.

In yet another embodiment, the toner may be prepared by forming an aqueous dispersion

comprising the water dispersible pigment and pigment grade magnetite (and optionally a water soluble image fixing material either alone or in admixture with a water soluble dye) and admixing the dispersion with hydrophobic silica particles in a high shear blender to obtain the desired particles in the form of an inner aqueous phase containing said pigment and magnetite (and said optional ingredient(s)) and encapsulated in an outer shell formed of said hydrophobic silica particles.

In a still further embodiment, the toner may be prepared by forming an aqueous dispersion comprising the water soluble dye, pigment grade magnetite and a water soluble image-fixing material and admixing the dispersion with hydrophobic silica particles in a high shear blender to obtain the desired particles in the form of an aqueous phase containing said dye, magnetite and image-fixing material and encapsulated in an outer shell formed of said hydrophobic silica particles.

The toners prepared in accordance with the present invention may also be used for the preparation of hectographic masters. For this purpose the colouring matter within the water droplets is preferably in the form of a saturated solution of a dye which is in addition alcohol soluble, in which case either the recording member or the receiving member as previously described may be used as a hectographic master. In those cases where the recording member is used as a hectographic master it is usually advantageous to evaporate the water contained in the image deposit prior to duplication to limit dye mobility during the duplication process.

The following Examples illustrate the present invention. However it should be realised that the Examples are intended to be read in the illustrative and not restrictive sense as those skilled in the art of electroscopic marking particle preparation will be able to adapt the teachings of the present disclosure to other materials without departing from the spirit of the invention as defined by the claims.

EXAMPLE 1

The aqueous phase component of a toner of the present invention was prepared from:-

crystal violet	15 grams
water (distilled)	300 grams

These components were placed into a Waring blender to which was then added

Hydrophobic silica, 7 millimicron mean particle size 450 grams

The mixture was blended in the Waring blender for 5 minutes to form an apparently dry free flowing powder of 10-40 microns particle size with a preponderance of particles of size within the range 20-30 microns.

The thus formed toner was used to develop a negative electrostatic latent image on a zinc oxide containing photoconductive recording member surface to produce a visible violet coloured image thereon.

The developed photoconductive recording member was contacted with a sheet of bond paper and the two contacting members were passed through the nip of a pair of pressure rollers. The nip pressure caused sufficient displacement of the hydrophobic silica outer layer of the toner particles to allow the dye containing aqueous phase to contact the bond paper receiving member surface and form a visible image thereon. The image on the bond paper receiving member surface was fixed thereon by evaporation of the water contained with the image deposit.

EXAMPLE 2

Example 1 was repeated with the crystal violet replaced with an equal weight of naphthalene black. Similar results were obtained but the transferred image was of black colour.

EXAMPLE 3

Example 1 was repeated, with the exception that the crystal violet was replaced with an equal weight of methylene blue. A high density transferred image was obtained.

EXAMPLE 4

Example 1 was repeated with the crystal violet replaced with an equal weight of disulphine blue. Similar results were obtained.

EXAMPLE 5

Example 1 was repeated with the crystal violet of Example 1 replaced with 4 grams of rose bengal. A pink image was obtained.

EXAMPLE 6

An aqueous pigment dispersion was prepared from:-

5	Hostaperm Black Colanyl pigment	10 grams	
	Distilled water	160 grams	5

These components were placed in a Waring blender, to which was added

10	Hydrophobic silica	300 grams	10
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The total blending time was 7 minutes. The so formed apparently dry free flowing toner was used as in Example 1. However the transferred image deposit was found to be inadequately fixed.

Hostaperm Black Colanyl pigment is a water-glycol dispersion of CI Pigment Black 6 containing 50% pigment by weight, manufactured by Hoechst. 15

EXAMPLE 7

Example 6 was repeated, with the exception that the pigment dispersion contained an equal weight of phthalocyanine blue pigment as a replacement for the CI Pigment Black 6.

EXAMPLE 8

20 A photoconductive recording member having a relatively hydrophilic surface was prepared by coating paper with the following composition:-
50 grams of Phenolphthalein were dissolved in:

25	Ethyl Alcohol	225 grams	
	Acetone	225 grams	25

and to the solution was added

30	Photoconductive Zinc Oxide	200 grams	30
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The resultant mixture was ball milled for 24 hours and then coated onto paper to form a photoconductive recording member having a relatively hydrophilic surface.

The thus prepared photoconductive recording member was electrostatically charged and exposed to form a latent electrostatic image thereon. The latent image was developed with the toner of Example 1. 35

The developed photoconductive recording member was then passed through the nip of a pair of pressure rollers, the surface of the roller contacting the developed recording member surface consisting of stainless steel.

A fixed image was produced on the photoconductive recording member surface. 40

EXAMPLE 9

Example 8 was repeated except that the surface of the pressure roller consisted of silicone rubber.

EXAMPLE 10

45 An aqueous pigment dispersion was prepared containing 45

	Hostaperm Black Colanyl Pigment	50 grams	
	Magnetite, pigment grade	50 grams	
	Distilled water	160 grams	

50 These components were placed in a Waring blender, to which was then added 50

	Hydrophobic silica	300 grams	
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55 The blending time was 7 minutes in total. The so formed apparently dry free flowing toner was used in a magnetic applicator to develop a negatively charged electrostatic latent image on a zinc oxide containing photoconductive recording member to produce a visible black coloured image thereon. The so formed image deposit was not suitable for pressure fixing. 55

EXAMPLE 11

60 Example 10 was repeated with the exception that 30 grams of polyethylene glycol were added to the water prior to blending. The so formed toner was used as in Example 10, but in this instance the image deposit could be fixed by the application of pressure. 60

EXAMPLE 12

An aqueous pigment/dye dispersion was prepared from:

	Hostaperm Black Colanyl Pigment	50 grams	
5	Magnetite, pigment grade	50 grams	5
	Crystal violet	12 grams	
	Distilled water	160 grams	
	Polyethylene Glycol	15 grams	

10 The dispersion was placed in a Waring blender, to which was then added 10

Hydrophobic silica 300 grams

The total blending time was 9 minutes. The thus formed toner was used as an Example 11 to form an image deposit which was fixed by the application of pressure. 15

EXAMPLE 13

An aqueous pigment/dye dispersion was prepared from:

	Crystal Violet	4.5 grams	
	Distilled water	85 grams	
20	Polyethylene Glycol	10 grams	20
	Magnetite, pigment grade	60 grams	

These components were placed in a Waring blender to which was then added

Hydrophobic silica 100 grams

25 The total blending time was 9 minutes. The thus formed apparently dry free flowing powder was used in a magnetic applicator to develop a positive electrostatic latent image on a cadmium sulphide photoconductive recording member constructed and operating as described in U.S. Patent No. 3,438,706. The image deposit formed was transferred electrostatically to a plain paper surface and pressure fixed thereto. 25

30 *EXAMPLE 14* 30

Example 13 was repeated with the polyethylene glycol replaced with 2 grams of propionic acid. Similar results were obtained.

EXAMPLE 15

35 Example 13 was repeated with the polyethylene glycol replaced with 10 grams of barium propionate. Similar results were obtained. 35

EXAMPLE 16

Example 13 was repeated with the polyethylene glycol replaced with 5 grams of glycerine. Similar results were obtained.

EXAMPLE 17

40 Example 13 was repeated with the polyethylene glycol replaced with 4 grams of an electroconductive resin containing quaternary ammonium groups. Similar results were obtained 40

EXAMPLE 18

45 Example 13 was repeated with the polyethylene glycol replaced with 30 grams of sucrose. Similar results were obtained. 45

EXAMPLE 19

Example 13 was repeated with the polyethylene glycol replaced with 30 grams of glucose. Similar results were obtained.

EXAMPLE 20

50 An aqueous pigment/dye dispersion was prepared as follows:- 50

	Nigrosine, water soluble	1.3 grams	
	Distilled water	25 grams	
	Glucose	17.5 grams	
55	Magnetite, pigment grade	26 grams	55

were blended together in a Waring blender to which was then added

60 Hydrophobic silica 100 grams 60

to form aqueous droplets containing dye, glucose, and magnetite pigment surrounded by an outer shell of hydrophobic silica. The total blending time was 10 minutes.

The thus formed toner was used as in Example 13 and similar results were obtained.

EXAMPLE 21

An aqueous pigment/dye dispersion was prepared as follows:-

5	Crystal violet	1.8 grams	
	Distilled water	33 grams	5
	Lactose	15 grams	
	Magnetite, pigment grade	30 grams	

were blended together and added in a Waring blender to

10	Hydrophobic silica	100 grams	10
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to form aqueous droplets containing dye, lactose, and magnetite pigment surrounded by an outer shell of hydrophobic silica. The total blending time was 10 minutes. The thus obtained toner was used as in Example 13 and similar results were obtained.

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EXAMPLE 22

Example 21 was repeated with the lactose replaced with an equal weight of tartaric acid. Similar results were obtained.

EXAMPLE 23

20 An aqueous pigment/dye dispersion was prepared as follows: 20

	Crystal violet	1.7 grams	
	Distilled water	33 grams	
	Fructose	22.5 grams	
25	Magnetite, pigment grade	34 grams	25

were blended together and added in a Waring blender to

30	Hydrophobic silica	100 grams	30
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to form aqueous droplets containing dry, fructose, and magnetite pigment, surrounded by an outer shell of hydrophobic silica. The total blending time was 10 minutes. The so formed toner was used as in Example 13 and similar results were obtained.

EXAMPLE 24

35 An aqueous pigment/dye dispersion was prepared as follows:- 35

	Nigrosine, water soluble	1.5 grams	
	Distilled water	28 grams	
	Sucrose	20 grams	
40	Magnetite, pigment grade	30 grams	40

were blended together and added in a Waring blender to

45	Hydrophobic silica	100 grams	45
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to form aqueous droplets containing dye, sucrose, and magnetite pigment surrounded by an outer shell of hydrophobic silica. The total blending time was 10 minutes. The so formed toner was used as in Example 13 and similar results were obtained.

EXAMPLE 25

50 Example 21 was repeated with the lactose replaced with an equal weight of maleic anhydride. 50

EXAMPLE 26

An aqueous pigment/dye dispersion was prepared as follows:-

55	Nigrosine, water soluble	1.75 grams	55
	Distilled water	33 grams	
	Succinimide	8.75 grams	
	Magnetite, pigment grade	26 grams	

60 were blended together and added in a Waring blender to 60

	Hydrophobic silica	100 grams	
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65 to form aqueous droplets containing dye, succinimide and magnetite pigment surrounded by an outer shell of hydrophobic silica. The total blending time was 10 minutes. The so 65

formed toner was used as in Example 13 and similar results were obtained.

There has been described a free flowing toner of high colour density which can be used for developing latent electrostatic images which may be subsequently transferred. The toner particles contain a harmless liquid and image fixing is possible as previously described without the use of heat fusing methods normally associated with dry development techniques. The toner causes reduced pollution.

WHAT WE CLAIM IS:

1. Electroscopic marking particles for the dry development of electrostatic latent images which particles comprise an inner aqueous phase encapsulated in an outer shell of hydrophobic silica, the aqueous phase containing a water soluble dye or a water dispersible pigment.
2. Electroscopic marking particles as claimed in claim 1 wherein said water soluble dye is crystal violet, disulphine blue, rose bengal, nigrosine, methylene blue or naphthalene black.
3. Electroscopic marking particles as claimed in claim 1 wherein said water dispersible pigment is CI Pigment Black 6 or phthalocyanine blue.
4. Electroscopic marking particles as claimed in any one of the preceding claims wherein the inner aqueous phase includes a water soluble or water dispersible image fixing material.
5. Electroscopic marking particles as claimed in claim 4 wherein the image fixing material is polyvinyl alcohol, ethylene glycol, polyethylene glycol, propionic acid, barium propionate, glycerine, an electroconductive resin containing quaternary ammonium groups, sucrose, glucose, lactose, fructose, maleic anhydride or succinimide.
6. Electroscopic marking particles as claimed in any one of the preceding claims which include from 50 to 200 parts by weight of said aqueous phase per 100 parts by weight of said hydrophobic silica.
7. Electroscopic marking particles as claimed in any one of the preceding claims wherein the aqueous phase additionally includes water dispersible magnetic particles.
8. Electroscopic marking particles as claimed in claim 7 wherein the magnetic particles are pigment grade magnetite.
9. Electroscopic marking particles as claimed in claim 1 substantially as hereinbefore described in any one of Examples 1 to 9.
10. Electroscopic marking particles as claimed in claim 1 substantially as hereinbefore described in any one of Examples 10 to 26.
11. A method of preparing electroscopic marking particles as claimed in claim 1 which method comprises dissolving the water soluble dye in water, and admixing the resultant solution with hydrophobic silica particles in a high shear blender to obtain the desired particles in the form of an inner aqueous phase containing said water soluble dye and encapsulated in an outer shell formed of said hydrophobic silica particles.
12. A method of preparing electroscopic marking particles as claimed in claim 1 which method comprises dissolving the water soluble dye and a water soluble image-fixing material in water, dispersing a water dispersible pigment in the resultant solution and admixing hydrophobic silica particles with the resultant dispersion in a high shear blender to obtain the desired particles in the form of an inner aqueous phase containing said water soluble dye, said water soluble image-fixing material and said pigment, and encapsulated in an outer shell formed of said hydrophobic silica particles.
13. A method of preparing electroscopic marking particles as claimed in claim 1 which method comprises dissolving a water soluble image-fixing material in water, dispersing in the resultant solution the water dispersible pigment, and admixing the resultant dispersion with hydrophobic silica particles in a high shear blender to obtain the desired particles in the form of an inner aqueous phase containing said water soluble image-fixing material and said pigment and encapsulated in an outer shell formed of said hydrophobic silica particles.
14. A method of preparing electroscopic marking particles as claimed in claim 1 which method comprises forming an aqueous dispersion comprising the water dispersible pigment and pigment grade magnetite and admixing the dispersion with hydrophobic silica particles in a high shear blender to obtain the desired particles in the form of an inner aqueous phase containing said pigment and magnetite and encapsulated in an outer shell formed of said hydrophobic silica particles.
15. A method according to claim 14 wherein the dispersion additionally includes a water soluble image-fixing material.
16. A method according to claim 15 wherein the dispersion additionally includes a water soluble dye.
17. A method of preparing electroscopic marking particles as claimed in claim 1 which method comprises forming an aqueous dispersion comprising the water soluble dye, pigment grade magnetite and a water soluble image-fixing material and admixing the

dispersion with hydrophobic silica material and admixing the dispersion with hydrophobic silica particles in a high shear blender to obtain the desired particles in the form of an inner aqueous phase containing said dye, magnetite and image-fixing material and encapsulated in an outer shell formed of said hydrophobic silica particles.

5 18. A method of preparing electroscopic marking particles as claimed in claim 1, substantially as hereinbefore described in any one of the foregoing Examples. 5

19. Electroscopic marking particles whenever prepared by the method claimed in any one of claims 11 to 18.

10 20. A method of developing an electrostatic latent image contained on a dielectric or photoconductive recording member surface which comprises the step of applying thereto electroscopic marking particles as claimed in any one of claims 1 to 10 or claim 19. 10

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