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(54) Toner.

(57) The present invention discloses a toner for electrophotography.

This toner comprises a surface tension reducing agent and a binder resin. Because the melt viscosity of the toner at a temperature of 200°C is 30 poises or more, a toner having an excellent void resistance can be obtained without a worsening of the fixability and blocking resistance thereof.

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(3.10/3.09/3.3.4)

The present invention is concerned with a toner used for developing an electrostatic latent image in, for example, electrophotography.

In the electrophotography field, the method described in U.S. Patent No. 229761 etc. is widely used. In this method, a uniform electrostatic charge is applied to a photoconductive insulator (Photocondrum, etc.) by corona charge, and an electrostatic latent image is formed by, e.g., light using various means. Then fine powder, i.e. toner, is electrostatically adsorbed on to the latent image thereby to develop the image and make it visible. If necessary, the toner picture image is transcribed onto a recording medium such as paper, and is fixed to the recording medium by, for example, pressure, heating, solvent vapour blasting or irradiation of light. The toner used for developing the electrostatic latent image includes particles obtained by pulverizing binder resin made of a natural or synthetic high molecular weight substance dispersing colorant such as carbon black. Usually the diameter of the toner particles is about 5 to 20 μm. The toner used for the development of an electrostatic latent image may consist of these particles alone, or may comprise the particles mixed with a carrier such as iron powder or glass beads.

Developing methods are either one-component developing methods or two-component developing methods. The toner used in the former method usually contains magnetic powder, which is frictionally charged by friction between the wall and the developing roller surfaces and is held on the developing roller by the magnetic force of a magnet incorporated in the roller. The toner is developed on to the latent image portion of a photoconductive insulator by the rotation of the roller, whereby the charged toner alone adheres to the latent image by electric attraction to carry the development of the image.

In the latter developing method, developer consisting of toner and carrier is frictionally charged by being mixed and stirred in a developing device. The toner is conveyed to the latent image portion of photoconductive insulator while being carried on the carrier, whereupon the charged toner alone is selectively adhered to the latent image by an electric attraction to carry out the development of the image.

A hot roller fixing method is conventionally employed for fixing the toner, although a flash fixing method utilizing light energy generated by a Xenon lamp is now under development. This method has the following favourable characteristics:

(1) The flash fixing method does not lower the resolution of the picture image because it is a non-contact fixing method.

(2) No waiting time is necessary after the current source is once switched off, and thus an immediate restart is possible.

(3) Even if the recording medium, such as copy paper, is jammed in a fuser due to a system malfunction, it will not burn.

(4) Any material and thickness of paper can be used as the recording medium, e.g., adhesive paper, preprinted forms, and sheets of paper with different thicknesses, etc.

The process by which a toner is fixed to a recording medium by the flash fixing method is explained as follows.

The toner transferred to a recording medium is adhered to the medium in powdered state and forms a picture image. At this stage, the image can be destroyed if rubbed with a finger. When light is irradiated onto the picture image by a Xenon lamp, the toner absorbs energy from the light. The temperature of the toner is accordingly elevated and the toner softens and melts and thus becomes closely adhered to the recording medium.

After the light has been extinguished, the temperature of the toner begins to fall and the toner solidifies, whereby a fixed picture image is formed.

A necessary condition for a toner is that the toner resin becomes soft at a comparatively low temperature and, at the same time, the picture image formed by the toner is not deformed even when the toner is in a molten state.

However, when a solid toner melts the viscosity thereof falls and the melted toner coagulates and deforms due to the surface tension thereof. In this case, the picture image formed by the toner will be deformed.

Low molecular weight polymers called oligomers are generally employed as a binder resin in a toner due to their low melting temperature and good thermal stability.

The oligomer, however, has defects such that a fixed picture image formed of such an oligomer is easily deformed due to the low melt viscosity and storage stability thereof, and thus the image quality is lowered. Further, when the light energy adsorbed by the toner is too strong, explosive fixing is liable which causes white voids called "image void", whereby the photographic density of the image is lowered.

Figures 1-(a), (b) and (c) of the accompanying drawings illustrate how image void is formed. These figures show that, when a strong light 3 (see Fig. 1(b)) is irradiated onto a toner 1 (see Fig. 1(a)) arranged in multiple columns on a sheet of recording paper 2, the toner 1 is easily melted due to the low softening temperature thereof, and a void 5 is formed inside the toner for the reasons described as follows. Note, numeral 4 in Fig. 1 represents a fixed picture image.

When the temperature of a part of toner 1 is elevated to the decomposition temperature thereof, a gas is produced, whereby a part of the toner protrudes, and thus a void 5 is formed.

The air in the empty spaces between the toner particles thermally expands and the toner protrudes, whereby a void 5 is formed.

The void 5 formed according to the above mechanism is formed by explosive fixing.

Even where the toner 1 absorbs energy strong enough to melt it, if the melt viscosity and storage stability of the binder resin 1 are too low compared with the surface tension thereof, the toner aggregates due to the surface tension thereof before the melted toner 1 solidifies, and thus a void 5 may be formed. The shorter the fixation time, i.e. the faster the printing speed of a printer or a copying machine, the greater the amount of energy irradiated in a short time is necessary to carry out fixing, and accordingly the more frequently the above void forming phenomenon occurs. This phenomenon becomes particularly conspicuous when a high speed machine with a processing speed of 700 mm/sec or more is employed.

One way of solving the above problems is to increase the molecular weight of the binder resin. Although the melt viscosity and storage elastic modulus of the toner 1 become higher, the melting point thereof also becomes higher, so that the fixability of toner 1 is decreased.

In light fixing, instantaneous light energy is given to the upper part of the accumulated toner 1. The heat generated by this energy is transmitted to the lower part of toner 1, and the fixing is conducted by melting of the lower part of the toner (refer to Japanese Patent Publication No. 55-140860). Namely, a temperature difference occurs between the upper part and the lower part of the toner 1; the lower part of the toner 1 having a comparatively low temperature. Accordingly, when the melting point of toner 1 is elevated, the lower part of toner 1 will not be substantially melted. Thus the fixability is extremely poor. When the thickness of the toner 1 accumulated by developing is greater, the above phenomenon becomes more conspicuous. When the thickness of toner 1 after the fixing exceeds 20 μm, good fixability cannot be maintained. It is, however, difficult always to maintain the thickness of toner 1 to be developed at a constant value.

Further, the toner 1 for the light fixing often uses a low molecular weight resin with a lower softening temperature than the polymeric binder resin used in the toner 1 for a hot roller fixing method. Thus a blocking phenomenon may occur such that the toner surface softens when exposed to a high temperature environment and the toners merge.

When the above blocking phenomenon occurs, the fluidity of the toner 1 becomes extremely low, and not only is the toner not smoothly supplied into the developing vessel but also the particle diameter, etc., thereof changes. Thus the electrification property of the toner also changes and a good developed image cannot be obtained.

Therefore, it has been necessary to develop an image 1 that exhibits a good fixability even if the amount of toner 1 thereof changes, and in which neither the formation of voids 5 nor a blocking phenomenon will occur.

As described above, in the toner resin for electrophotography in which a light fixing system is used, an epoxy resin represented by bisphenol A diglycidyl ether, etc is employed as the binder. When such a resin is to be used as a binder resin, it has been necessary to employ an oligomer with a low softening temperature, i.e. a comparative low molecular weight, to achieve good fixability. Such an oligomer is liable to cause explosive fixation due to thermal decomposition thereof, and has a defect such that, owing to the high surface tension and melt viscosity thereof, voids are produced due to the aggregation of the toner particles and the image quality is lowered. Further, the blocking phenomenon occurs when the toner is exposed to a high temperature environment.

To solve these problems, it is necessary to increase the melt viscosity of the binder resin but not to produce any white voids due to movement of the binder resin. As a means of increasing the melt viscosity of the binder resin, the following methods are considered:

(1) increase the degree of polymerization of the binder resin.

(2) introduce a comparatively long side chain containing 4 or more carbon atoms into the main chain structure of the binder resin.

(3) introduce a cross-link between the main chain structures of the binder resin.

In methods (1) and (3), however, although the melt viscosity of the binder resin may be increased, the melting point thereof is also elevated. Therefore, although void formation may be prevented, the fixability is often degraded. In method (2), although the melt viscosity of the binder resin may be increased without elevating the melting point thereof, the blocking resistance is often greatly worsened, and the glass transition point of the binder resin is lowered in this case.

The present invention has been created in order to solve the problems as described above, and the object thereof is to provide a novel toner having an excellent void forming resistance without lowering the fixability and blocking resistance thereof.

The present inventors studied the afore-described problems, and found that these problems could be solved by adopting a binder resin with certain physical property values.

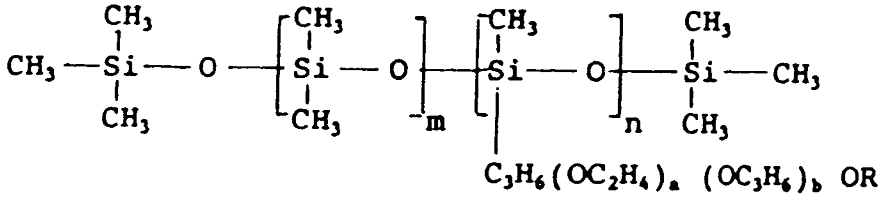
According to the present invention, there is provided a toner comprising a surface tension reducing agent and one or more binder resins, characterized in that the melt viscosity and the surface tension of said toner, at a temperature of 200 ° C are, respectively, 30 poises or more and below 15 dyne/cm.

The present inventors found after intensive studies that, even when a binder resin with a comparatively low melt viscosity is employed to prevent the lowering of the fixability of a binder resin accompanying the elevation of the melting point thereof and the lowering of blocking resistance thereof accompanying the lowering of the glass transition point thereof, void formation arising from aggregation can be controlled by employing at least a substance for lowering the surface tension of the binder resin or an intermolecular force acting between the molecules constituting the binder resin, i.e., by employing a toner having its surface tension diminished by dispersing a surface tension decreasing agent in the binder resin, and thus achieved the present invention.

The present invention is now explained more in detail.

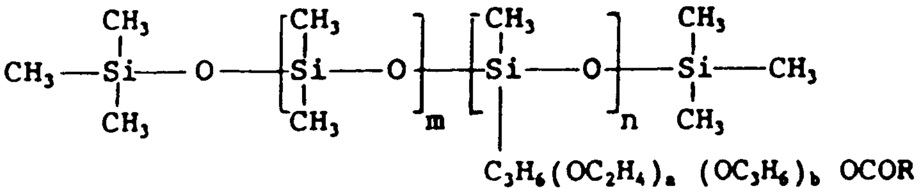
The present invention is concerned with a toner containing binder resins, in which a surface tension lowering agent is contained and as the surface tension decreasing agent, there may be employed a non-ionic surface active agent.

As a polymer to be used as the surface tension reducing agent, there may be employed a surface active agent having hydrophilic and hydrophobic groups and exhibiting surface activity e.g.
polydimethylsiloxane-polyether,
polydimethylsiloxane-polyester represented by the following general formulae:



$$CH_3-Si(CH_3)_2-O-\left[Si(CH_3)_2-O\right]_m-\left[Si(CH_3)(C_3H_6(OC_2H_4)_a(OC_3H_6)_b\,OR)-O\right]_n-Si(CH_3)_2-CH_3$$

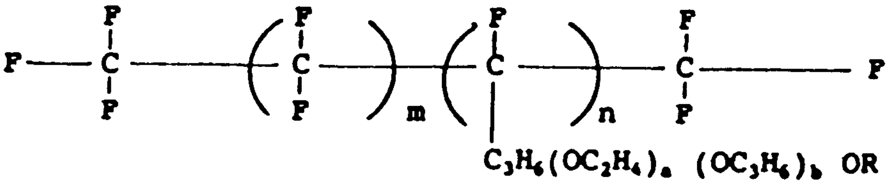
R: an alkyl group or H
$0.1 < b/a < 10$



$$CH_3-Si(CH_3)_2-O-\left[Si(CH_3)_2-O\right]_m-\left[Si(CH_3)(C_3H_6(OC_2H_4)_a(OC_3H_6)_b\,OCOR)-O\right]_n-Si(CH_3)_2-CH_3$$

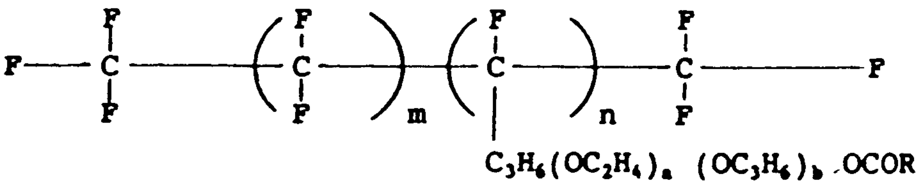
R: an alkyl group or H,
$0.1 < b/a < 10$,

or fluorine polymers represented by the following formula



$$F-CF_2-\left(CF_2\right)_m-\left(CF(C_3H_6(OC_2H_4)_a(OC_3H_6)_b\,OR)\right)_n-CF_2-F$$

R: an alkyl group or H
$0.1 < a/b < 10$,



$$F-\overset{F}{\underset{F}{C}}-\left(\overset{F}{\underset{F}{C}}\right)_m\left(\overset{F}{\underset{C_3H_6(OC_2H_4)_a\,(OC_3H_6)_b\cdot OCOR}{C}}\right)_n\overset{F}{\underset{F}{C}}-F$$

R: an alkyl group or H
0.1 < a/b < 10

etc. may be employed.

The silicone polymer used as the surface tension reducing agent may be added to the binder resins at the stage of polymerizing the binder resins from monomers or at the stage of melting and kneading the toner-constituting materials. However, where the surface tension reducing agent is added to the binder resins at the stage of the polymerization of the binder resins, the surface tension reducing agent must be a material that does not impede the polymerization of the binder resins and that does not induce a secondary reaction.

In addition, the number-average molecular weight of the silicone polymer is preferably from 5×10^2 to 5×10^4, and as the number average molecular weight is increased, the dispersibility of the silicone polymer into the binder resins is lowered.

Although the amount of added surface tension reducing agent is determined according to the material of the surface tension reducing agent and the surface tension of the binder resins, the surface tension is preferably below 15 dyne/cm at a temperature of 200 °C when a polyester resin (polyethylene terephthalate) is employed, which value corresponds to 0.01 to 2.00 wt% based on the weight of the toner. The reason why the amount of added silicone polymer should be below 2.00 wt% is that, if the amount exceeds this limit, due to the surface tension reducing agent's effect of lowering the melt viscosity of the binder resin, the melt viscosity thereof becomes too low and therefore the void formation preventing ability thereof is lowered. In addition, the reason why the lower limit of the amount of added silicone polymer should be 0.01 wt% is that, if the amount is below said value, the void formation preventing ability resulting from the lowering of the surface tension cannot be obtained.

There may be employed as a non-ionic surface active agent other than the pendant type silicone polymer, polyethylene glycol ether or polyethylene glycol polyester represented by the following formula

$RCOO\,(CH_2\,CH_2\,O)_n\,OR'$

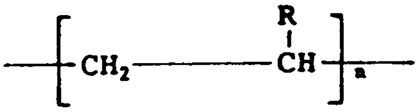
wherein R and R', respectively, indicates an alkyl group or a hydrogen atom and $40 \geqq n \geqq 10$ or

$RCOO\,(CH_2\,CH_2\,O)_n\,COR'$,

wherein R and R', respectively, indicates an alkyl group or a hydrogen atom and $40 \geqq n \geqq 10$. When these aliphatic non-ionic surface active agents are employed, it is necessary to add them in a proportion of 5 wt% or more (normally within the range of from about 10 to about 20 wt%) to reduce the surface tension to a sufficient degree. In the above case, although the surface tension is reduced simultaneously with the addition of the non-ionic surface active agent, the melt viscosity is also markedly lowered, so that the void formation preventing ability is also degraded. Therefore, the amount of polyethylene glycol ether or polyethylene glycol ester should be below 50 wt%.

As the polyethylene glycol ether or polyethylene glycol ester used as the surface tension reducing agent is hydrolysed under high temperature conditions, it is impossible to add it to and disperse it in the binder resin when synthesizing the binder resin.

In addition, polyethylene wax and polypropylene wax (number average molecular weight: 2×10^3 to 2×10^4) represented by the following general formula



$$-\left[CH_2-\overset{R}{CH}\right]_a-$$

wherein R is a hydrogen atom or group CH_3 may be employed as the surface tension reducing agent.

In the above case, to reduce the surface tension to a sufficient degree and prevent void formation, the amount of added surface tension reducing agent should be from 2 to 20 wt%.

As toner binder resin used in the present invention, any employable for electrophotography, e.g., styrene acryl, epoxy resin, polyester resin, etc., may be employed independently or in combination. When a binder resin with a surface tension reducing agent dispersed therein is combined with another binder resin, a binder resin mixture with a surface tension reducing agent added only to one binder resin may be employed, as long as a required amount of surface tension reducing agent is added to the whole of the binder resin mixture.

The toner employed in the present invention may be produced by a known process. That is, binder resins, a colouring agent, surface tension decreasing agent, carbon, an charge control agent etc. are melted and kneaded by, e.g., a pressure kneader, roll mill, extruder, etc., and thereby dispersed uniformly, following which the uniformly dispersed mixture is finely pulverized, e.g., by a jet mill etc., and the thus obtained powder is classified by a classifier such as an air classifier to thereby obtain the desired toner.

The various physical properties were determined by the following measuring methods.

(1) Surface tension

Surface tension is the value determined at a temperature of 200 °C by employing a Wilhelimie method surface tension measuring equipment equipped with a constant-temperature sample holder with a temperature controlling range of + 0.5 °C, "Digiomatic ESB-V" (manufactured by Kyowa Kagaku K.K.).

(2) Melt viscosity/storage modulus

Melt viscosity and storage modulus are values obtained by the measurement of a temperature rise from 50 °C to 250 °C at a programming rate of 10 °C/min in a nitrogen atmosphere by employing a cone plate type dynamic viscoelasticity measuring equipment, "MR-3 Soliquid Meter [phonetic]" (manufactured by K.K. Rheology). Note, the frequency in this case was set as 0.5 Hz.

The invention will now be described with reference to the following Examples.

Example 1

First, to 92 parts by weight of an epoxy resin (bisphenol A glycidyl ether; epoxy equivalent: 900 to 1000) as binder resin, there were added 0.5 parts by weight of a pendant type silicone polymer (produced by Nihon Unitica Co., Ltd.) as a surface tension decreasing agent, and as colorants, 5 parts by weight of carbon black ("Black Pearls L" produced by Cabot Co., Ltd.; average particle diameter: 0.024 µm, specific surface area: 138 m^2/g) and 3 parts by weight of nigrosine dye (Oil Black BY produced by Orient Kagaku K.K.). The obtained mixture was melted and kneaded in a pressure kneader for 30 min, at a temperature of 130 °C, so that a toner cake was obtained, and the toner cake was cooled and pulverized by a rotoprex pulverizer to obtain a rough granular toner with a particle diameter of about 2 mm.

Subsequently, the rough granular toner was finely pulverized by a jet mill ("PJM Pulverizer" produced by Japan Newmatic Co., Ltd.) and the thus obtained powder was classified by an air classifier (produced by Alpine Co., Ltd.), so that a positively charged toner (Toner A) with a particle diameter of from 5 to 20 µm was obtained.

Subsequently, a developer, consisting of 5 parts by weight of toner A and 95 parts by weight of amorphous iron powder, "TSV 100/200" (produced by Nihon Teppun K.K.) was prepared as carrier and with the prepared developing agent, a printing test was carried out by employing an improved "FACOM-6715" laser printer and the optical density of the obtained picture image was determined. The judgement of void formation states was conducted visually. The surface tension of the toner was determined at a temperature of 200 °C by employing surface tension measuring equipment ("Digiomatic ESB-V" manufactured by Kyowa Kagaku K.K.). The result of the printing test showed that toner A had an excellent void resistance and a printing density of 1.1, and that the surface tension of toner A was 15 dyne/cm. (refer to the added Table).

Example 2

First, to 92 parts by weight of polyester (polyethylene terephthalate; weight-average molecular weight: 1000) with 1.0 part by weight, based on the weight of the resin, of silicone polymer added, said polyester being employed as the binder resin, there were further added 5 parts by weight of carbon black and 3 parts by weight of nigrosine dye as colorants. The obtained mixture was melted and kneaded in a pressure kneader for 30 min. at a temperature of 130°C, so that a toner cake was obtained. The obtained toner cake was cooled and was converted into a rough granular toner with a particle diameter of about 2 mm, by a rotoprex pulverizer.

Subsequently, the obtained rough granular toner was finely pulverized by a jet mill and the obtained powder was classified by an air classifier, so that a positively charged toner (Toner B) with a particle diameter of from 5 to 20 pm was obtained.

The result of the printing evaluation showed that toner B had an excellent void resistance. The optical density was 1.2, and the surface tension of toner B was 13 dyne/cm (refer to the table).

Example 3

First, employing as binder resins 62 parts by weight of styrene acryl with 2.0 parts by weight, based on the resin weight, of silicone polymer added and 30 parts by weight of a polyester resin (polyethylene terephthalate; weight-average molecular weight: 1000) with no silicone polymer added, 3 parts by weight of carbon black (Black Pearls L) and 3 parts by weight of nigrosine dye were further added as colorants to the binder resins. The obtained mixture was melted and kneaded by a pressure kneader for 30 min at a temperature of 130°C, so that a toner cake was obtained. Subsequently, the obtained toner cake was cooled and pulverized into a rough granular toner with a particle diameter of about 2 mm by a rotoprex pulverizer.

Then, the obtained rough granular toner was finely pulverized by a jet mill (PJM pulverizer) and the obtained fine powder was classified by an air classifier (manufactured by Alpine Co., Ltd.), so that a positively charged toner (Toner C) with a particle diameter of from 5 to 20 μm was obtained.

The result of the printing evaluation showed that toner C had an excellent void resistance. The optical density of 1.3, and the surface tension of toner C was 10 dyne/cm (refer to the table).

Comparative Example 1

Example 1 was repeated except that, at the time of melting and kneading the toner, silicone polymer was not added as a surface tension reducing agent, so that a toner D was obtained. When a printing test and the determination of surface tension of the toner were carried out in the same way as in Example 1, many voids were formed during the printing of this toner and the printing density was 0.8. The surface tension of toner D was 25 dyne/cm (refer to the table).

Comparative Example 2

Example 2 was repeated except that silicone polymer was not added as a surface tension reducing agent, so that a toner E was obtained. When a printing test and the determination of surface tension of the toner were carried out in the same way as in Example 1, many voids were formed during the printing of this toner and the printing density was 0.7. The surface tension of toner E was 23 dyne/cm (refer to the added table).

Comparative Example 3

Example 1 was repeated except that 92 parts by weight of an epoxy resin were employed as binder resin and 3 parts by weight of silicone polymer were added thereto as a surface tension reducing agent, so that toner F was obtained. When a printing test and the determination of surface tension of the toner were carried out in the same way as in Example 1, very many voids were formed during the printing of this toner and the printing density was 0.7. The surface tension of toner F was 9 dyne/cm (refer to the added table).

Comparative Example 4

Example 3 was repeated except that silicone polymer was not added to styrene acryl as a surface tension reducing agent, so that a toner G was obtained. When a printing test and the determination of surface tension of the toner were carried out in the same way as in Example 1, many voids were formed in the printing of this toner and the printing density was 0.6. The surface tension of toner G was 33 dyne/cm (refer to the added table).

Table

Evaluation of toners prepared as samples							
	Example 1	Example 2	Example 3	Comparative Example 1	Comparative Example 2	Comparative Example 3	Comparative Example 4
Binder resin	epoxy	polyester	polyester styrene -acryl	epoxy	polyester	expoxy	polyester styrene-acryl
Amount of added surface tension decreasing agent	0.5	1.5	2.0	0	0	3.0	0
Surface* tension	15	13	10	25	23	9	33
Void formation preventing characteristic	○	○	○	x	x	x	x
Printing density	1.1	1.2	1.3	0.8	0.7	0.7	0.6
Melt viscosity *	30	30	50	50	50	20	90

* : Measured values at a temperature of 200 ° C

As explained above, according to the present invention, a toner excellent in void resistance may be obtained without worsening the fixability and blocking resistance thereof.

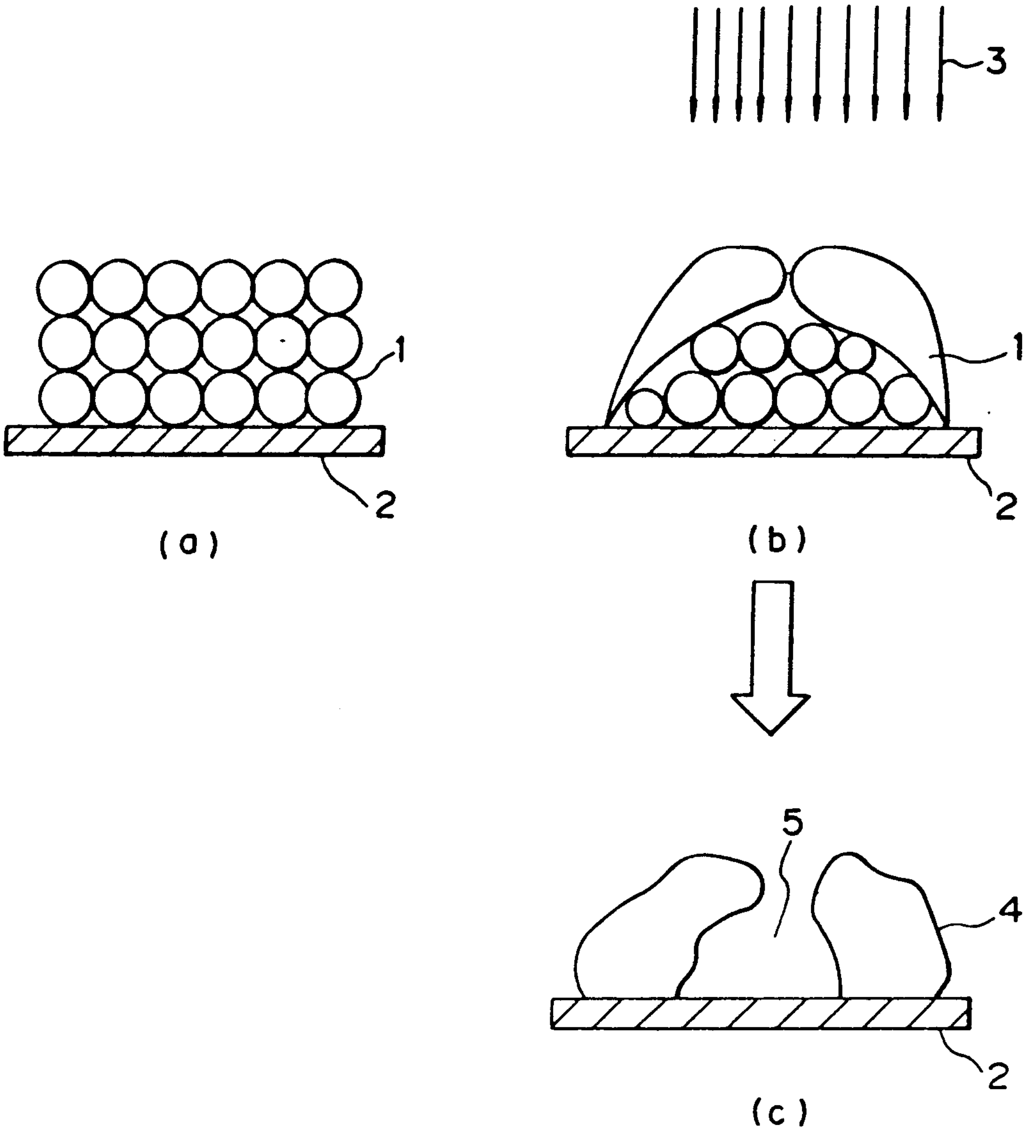
Claims

1. A toner comprising a surface tension reducing agent and one or more binder resins, characterized in that the melt viscosity and the surface tension of said toner, at a temperature of 200 ° C are, respectively, 30 poises or more and below 15 dyne/cm.

2. A toner according to Claim 1, characterized in that said surface tension reducing agent is a non-ionic surface active agent.

3. A toner according to Claim 2, in which said non-ionic surface active agent is silicone polymer or a fluoric polymer.

Fig. 1



European Patent
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EUROPEAN SEARCH REPORT

Application Number
EP 94 11 4757

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.5)
X	FR-A-2 386 847 (MITA) * page 9, line 1 * * page 10, line 15 - line 28 * * page 22; example 1 * * claims 1,2,6,7,11 * ---	1-3	G03G9/087
X	US-A-4 198 477 (WILLIAMS ET AL.) * column 3, line 21 - line 37 * * column 3, line 52 * * column 5, line 61 - line 62 * ---	1-3	
X	DE-A-30 39 224 (DAIKIN KOGYO) * page 18, paragraph 3; claims 1,2 * -----	1-3	
			TECHNICAL FIELDS SEARCHED (Int.Cl.5)
			G03G

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	17 November 1994	Vogt, C

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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A : technological background
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