UV curable toner particles and toners and developers comprising these

Dry toner particles are described comprising: at least a UV curable resin, and a coloring agent, wherein the UV curable resin has a Tg > 45°C, the toner particles comprising the radiation curable resin have a Tg > 40°C, the temperature resistance of the toner particles when fused and cured is larger than 50°C, and the particle size of the toner particles is between 4 and 14μm.

The toner particles can be used in a coloured toner for printing using a suitable printing device onto a substrate. The resin is cured either in-line, e.g. at the time of fusing the toner to a substrate or off-line.
Description

[0001] The present invention relates to particles for curable toners for printing as well as to toners and developers comprising the particles themselves, to apparatus and methods for printing the toners and for curing the toners.

Background of the invention

[0002] In imaging methods like electro(photo)graphy, magnetography, ionography, etc. a latent image is formed which is developed by attraction of so called toner particles. Afterwards the developed latent image (toner image) is transferred to a final substrate and fused to this substrate.

[0003] Toner particles are basically polymeric particles comprising a polymeric resin as a main component and various ingredients mixed with said toner resin. Apart from colorless toners, which are used e.g. for finishing function, the toner particles comprise at least one coloring substance such as black and/or other coloring substances, e.g., colored pigment.

[0004] In the beginning color electro(photo)graphy was mostly used for producing colored images (e.g. graphic arts, presentations, colored books, dissertations). When the process speed of producing digital colored images increases, other more productive applications also became feasible (direct mailing, transactional printing, packaging, label printing, security printing). This means that after the action of being produced by electro(photo)graphy, the toner images further have to withstand some external factors applied during the subsequent treatments. The problems associated with multiple, superimposed layers of toner particles that are in one way or another fixed on a substrate are manifold, not only with respect to image quality but also with respect to image stability and with respect to mechanical issues.

[0005] An example of high mechanical impact on the toner layers is sorting of printed papers (e.g. direct mail applications). The fast turning wheels of a sorting machine can give a temperature increase above the glass transition temperature (Tg) of the resin used, which can cause contamination with pigmented toner resin on the next coming papers. Another application where the heat and mechanical resistance of the toner layer is stressed is the production of e.g. car manuals. When the temperature inside the car rises above the Tg of the toner resin (e.g. when parked in the sun), the papers in the manual can stick to each other.

[0006] In the case of printing packaging materials with the use of toner technology, increased temperatures can be dealt with in many ways. Plastics can be used as a substrate and bags made out of it with the use of a sealing apparatus. If the sealing temperature is above the Tg of the used toner resin, the toner images get disturbed or distorted.

[0007] For a lot of these applications, a toner resin with a higher Tg and Tm should be used, but then the amount of energy necessary to fuse the toner particle onto the substrate would be so high that the application is energetically not interesting anymore. Secondly a lot of substrates can't be used anymore. High Tg toners exist already, but the demand for high speed print engines increases the demand for toner particles which can be fused at lower temperatures at a very high speed.

[0008] The use of a transparant covercoat made out of radiation curable toner particles has been described already in e.g. US5905012 to protect an image produced by electrophotography to improve the weather resistance of an image produced by means of electrophotography.

[0009] A non-image wise transparant UV curable coating has been described already in European Patent Application EP02078520.0 and US Patent Serial No. US10/226636 to give a flexible, high gloss finishing to printed papers both of which are incorporated herein by reference.

[0010] Prints obtained by means of electrophotography and by the use of thermally fixable toner are thermal stable only to approximately 100°C. Packaging materials must however partly be heated to temperatures far above 100°C during the production of sealed packaging. For example, for sealable packaging, a completely transparent, heat resistant cover layer from a toner hardening by UV light has been described in EP1186961.

[0011] The use of UV curable pigmented powders is already well known in the field of powder coatings (e.g. EP792325), but there are some major differences with respect to the field of toners. The size of the particles (6-10 microns for toner versus >30 microns for powder coatings) and the particle size distribution are quite different. Also the thickness of the layers applied with powder coatings is at least a factor 3 to 4 times thicker in comparison with the toner images. The speed of fusing and curing is very low compared, for example, to the high speed printers which are now available in the field (e.g. Igen3, Xeikon DCP500D). Powder coatings are also never applied imagewise. The powders are charged by some means and brought onto the surface of the material, which has to be coated. This is all quite different from toner, which is brought either directly imagewise on a substrate, or via a latent image on a photoconductor to a substrate.

[0012] In US7212526 a UV curable liquid toner has been described to improve the adhesion of the cured toner to the final substrate rather than to the surface of the image receptor during the transfuse step instead of withstanding high temperatures. The curing here takes place during the transfer step from photoreceptor to paper.

[0013] In US5470683 (Kouji Inaishi) discloses the use of a UV-curable toner in a completely different way of making
images. Three types of toners are mixed and are placed in an equal amount onto a temporary polyester film. By making use of visible light some toner particles are selectively cured which then stick to the polyester film. The non-cured toner is then further transferred (by applying pressure) from the polyester to the final paper image carrier. This is not an example of electrophotography and the final image on paper is afterwards not cured.

CA2085546 makes use of a UV curable under layer in order to increase the adhesion of the toner image after fusing. Also here no (UV)-curing takes place after the toner image has been formed.

US 2002/0090238 (Bartscher et al.) discloses influencing the degree of luster (gloss) by making use of UV-curable toner. From the teaching it is not clear why a UV carable toner should be necessary because it seems that the gloss is mainly adjusted during the fusing step, a method that is commonly known to those skilled in the art. Also, when the fusing degree of the resin is too low, the UV-curing never comes to the same degree in comparison to a curing process which took place when the toner particles have been fully fused and thus having their lowest viscosity. This way of working (establishing the degree of luster by the control of the fusing temperature) gives no solution to solvent resistance and to heat resistance, especially when low gloss values are wanted.

There is still a need to provide a toner which can be fixed at low temperatures but which is resistant to high temperatures once printed while maintaining all the other properties necessary to function correctly in a printer.

Objects and summary of the invention

It is an object of the invention to provide a toner to produce images that are resistant to high temperatures.

It is a further object of the invention to provide a toner for forming toner images wherein said toner is resistant to mechanical abrasion.

It is a further object of the invention to provide a toner for producing toner images that are resistant to the influence of common organic solvents.

In one aspect, the current invention does not apply a radiation curable toner as a post finishing layer during an extra step, but the toner used for the image itself is radiation curable. The advantage of UV curable toner for the image instead of applying a covering coating above the conventional toner image is that the printed image itself is better protected against high temperature treatments, long after the image formation takes place.

The present invention provides dry toner particles comprising:

- at least a UV curable resin, and
- a coloring agent, wherein:
  - the UV curable resin has a Tg > 45°C
  - the toner particles comprising the radiation curable resin has a Tg > 40°C,
  - the temperature resistance of the toner particles when fused and cured is larger than 50°C,
  - the particle size of the toner particles is between 4 and 14µm.

The particles may also comprise a photoiniator. The UV curable resin may be a polyester resin, for example. The temperature resistance of the fused and cured toner particles is preferably larger than >80°C. The particle size of the toner particles is preferably between 5 and 10µm. The viscosity of the toner particles is preferably between 100 and 1500 Pa.s. The solvent resistance of the fused and cured toner particles is preferably greater than 7 MEK rubs. The abrasion resistance of the fused and cured toner particles is preferably lower or equal to 3.

The present invention also provides a dry electrostatographic developer composition comprising carrier particles and toner particles according to any of the wherein

- said carrier particles comprise a core particle coated with a resin in an amount of 0.4 tot 2.5%,
- the absolute charge expressed as fC/10µm (q/d) is between 3 and 13 fC/10µm.

The present invention also provides a method of fusing and curing dry toner particles, comprising:

- selectively imagewise depositing radiation curable toner particles on a substrate to form an image comprising areas of deposited toner and areas of no deposited toner,
- fusing the toner particles on the substrate, and
- radiation curing the fused toner.

The present invention also provides a substrate printed with toner particles which have been fused and cured. The fusing and curing can be done in-line or off-line. The radiation curing is preferably with UV light. The UV dose is preferably between 3 and 30 J/cm². The substrate is preferably a polymeric or plastic foil.

Further objects and advantages of the present invention will become evident from the detailed description
Detailed description of the invention

[0024] The present invention will be described with reference to certain embodiments but these are provided by way of example only. The skilled person will appreciate that the invention may have wide application as indicated in the attached claims.

[0025] In one aspect, toner particles according to embodiments of the present invention may comprise the radiation curable resins (radiation curable compounds or compositions) that preferably are UV-curable resins as sole toner resin, or the radiation curable resins may be mixed with other toner resins. It is not anticipated that there are severe restrictions on the additional toner resins so that all toner resins, known in the art may be considered useful for the production of toner particles according to this invention. The resins mixed with the radiation curable resins can be polycondensation polymers (e.g. polyesters, polyamides, co(polyester/polyamides), etc), epoxy resins, addition polymers or mixtures thereof.

[0026] The term "radiation curable" should be interpreted widely to include forms of radiation such as ultra-violet light, and also high energy radiation or particles such as electron beams, X-rays, etc. Although electron beam curable compounds can be used in the present invention, the radiation curable groups are preferably curable by UV-light. The present invention, the radiation curable groups are preferably curable by UV-light.

[0027] Useful radiation curable polymeric compounds, in toner particles for use in the present invention are UV curable solid epoxy resins with a glass transition temperature of $T_g \geq 40^\circ C$ as disclosed, for example, in EP667381B1 which is incorporated herein by reference. Glass transition temperature is preferably determined in accordance with ASTM D3418-82. Other useful UV curable resins for incorporation in toner particles, according to this invention are toners based on unsaturated polyesters and polyurethane acrylates. The term polyester includes all polymers with a backbone structure based on a polycondensation of an alcohol and an acid. Other suitable UV curable resins are unsaturated polyesters based on terephthalic acid and neopentylglycol available form UCB Chemicals under the trade-name Uvecoat. Another binder system useful in the present invention, e.g. a toner composed of a mixture of an unsaturated polyester resin in which maleic acid or fumaric acid is incorporated and a polyurethane containing a vinyl ether available form DSM Resins under the trade name “Uracross”.

[0028] In a preferred embodiment the glass transition temperature of said polymers is above $45^\circ C$ and the $T_g$ of the toner is higher than $40^\circ C$.

[0029] For one form of UV curing to proceed it is necessary that a photoinitiator is present. Useful photoinitiators in the context of this invention, are compounds I, II and III or mixtures of these compounds, the structural formulas are shown below:

- Compound I: 1 hydroxy-cyclohexyl phenyl ketone
- Compound II: bis (2,4,6 trimethylbenzoyl)-phenyl- phosphine oxide
- Compound III: 2,2 dimethoxy-1,2 - diphenyl 1 ethanone. Commercially available photoinitiators are available from Ciba Geigy under the tradename Irgacure.

![Compound I](image)

![Compound II](image)

![Compound III](image)
Carrier particles can be either magnetic or non-magnetic. Preferably, the carrier particles are magnetic particles. Suitable magnetic carrier particles have a core of, for example, iron, steel, nickel, magnetite, γ-Fe₂O₃, or certain ferrites such as for example CuZn and environmental friendly ferrites with Mn, MnMg, MnMgSr, LiMgCa and MnMgSn. These particles can be of various shapes, for example, irregular or regular shape. Generally these carrier particles have a median particle size between 30 and 65µm. Exemplary non-magnetic carrier particles include glass, non-magnetic metal, polymer and ceramic material. Non-magnetic and magnetic carrier particles can have similar particle size.

Preferably the carrier core particles are coated or surface treated with an organic or an inorganic material or resin, for example in a concentration of 0.4 to 2.5% to obtain, for example, desirable electrical, triboelectrical and/or mechanical properties.

In the two-component developer the amount of UV curable toner particles can be, for example, between about 1 and about 10 wt.% (relative to the amount of developer).

Tribo-electric charging of the toner particles proceeds in so-called two component developer mixtures by means of the carrier particles. Charging of individual toner particles through triboelectricity is a statistical process, which will result in a broad distribution of charge over the number of toner particles in the developer. If a relative large
The substrate to print the UV curable toner on, can be any suitable printing substrate, e.g. paper, plastic, textiles and metal foils and combinations of them in different thicknesses. In an apparatus according to the present invention, the radiation curing curable resin and thus the means for radiation curing the toner particles comprise are means for UV-curing (UV-light, g., infrared radiation (IR-radiation), is preferred.

The means for fusing said toner particles according to this invention can be contact (e.g. hot-pressure rollers) or non-contact means. Non-contact fusing means according to this invention can include a variety of embodiments, such as: (1) an oven heating process in which heat is applied to the toner image by hot air over a wide portion of the support sheet, (2) a radiant heating process in which heat is supplied by infrared and/or visible light absorbed in the toner particles, the light source being e.g. an infrared lamp or flash lamp. According to a particular embodiment of "non-contact" fusing of sheets.

The radiation curing can proceed off-line in a separate apparatus wherein the fused layer of toner particles is heated again and irradiated with curing rays. It is particularly preferred that the radiation (UV) curing proceeds on the molten toner and particularly while the toner receiving layer has some fluidity. Preferably the radiation curing proceeds at a temperature that preferably is at most 150°C, that have a melt viscosity at 120°C between 50 and 2000 Pa.s, preferably between 100 and 1500 Pa.s.

The means for fusing said toner particles to the substrate can be any means known in the art. For example, the means for fusing toner particles according to this invention can be contact (e.g. hot-pressure rollers) or non-contact means. Non-contact fusing means according to this invention can include a variety of embodiments, such as: (1) an oven heating process in which heat is applied to the toner image by hot air over a wide portion of the support sheet, (2) a radiant heating process in which heat is supplied by infrared and/or visible light absorbed in the toner particles, the light source being e.g. an infrared lamp or flash lamp. According to a particular embodiment of "non-contact" fusing the heat reaches the non-fixed toner image through its substrate by contacting the support at its side remote from the toner image with a hot body, e.g., a hot metallic roller. In the present invention, non-contact fusing by radiant heat, e. g., infrared radiation (IR-radiation), is preferred.

In a contact fusing process, the non-fixed toner images on the substrate are contacted directly with a heated body, i.e. a so-called fusing member, such as fusing roller or a fusing belt. Usually a substrate carrying non-fixed toner images is conveyed through a nip formed by establishing a pressure contact between said fusing member and a backing member, such as a roller. To obtain high quality images, it is recommended to use hot roller systems with a low amount of release agents.

In an apparatus according to the present invention it is preferred to use toner particles comprising a UV-curable resin and thus the means for radiation curing the toner particles comprise are means for UV-curing (UV-light emitters as e.g. UV lamps). In an apparatus according to the present invention, it is preferred that the radiation curing proceeds in-line with the printing. Therefore, it is preferred that said means for fusing said toner images emit infrared radiation (are infra-red radiators) and said means for UV curing (e.g. one or more UV emitting lamps as, e.g. high
pressure mercury lamps) are installed immediately after said fusing means so that the UV curing proceed on the still molten toner image. A combination of infra-red radiators (the means for fusing the toner particles) and UV emitting lamps (the means for radiation curing) in a single station (a fixing/curing station), so that the fusing and the radiation curing proceed simultaneously, is also a desirable design feature of an apparatus according to this invention. The apparatus according to the present invention can comprise if so desired, more than one fixing/curing station. The UV emitting means are preferably UV radiators with a capacity (an intensity) between 25 W/cm and 250 W/cm in order that the UV curing is done with at most 30J/cm².

[0052] The means for image-wise depositing toner particles can, in apparatus according to this invention, also be direct electrostatic printing means (DEP), wherein electrodes.

[0053] Said means for image-wise depositing toner particles can also be toner depositing means wherein first a latent image is formed. In such an apparatus, within the scope of the present invention, said means for image-wise depositing toner particles comprise:

• i) means for producing a latent image on a latent image bearing member,
• ii) means for developing said latent image by the deposition of said toner particles, forming a developed image, and
• iii) means for transferring said developed image onto a substrate.

Said latent image may be a magnetic latent image that is developed by magnetic toner particles (magnetography) or, preferably, an electrostatic latent image. Such an electrostatic latent image is preferably an electrophotographic latent image and the means for producing a latent image are in this invention preferably light emitting means, e.g., light emitting diodes or lasers and said latent image bearing member comprises preferably a photoconductor.

Test methods

Charge measurement of toner particles

[0054] The charge is measured with a q/d meter from Dr. R. Epping PES Laboratorium D 8056 Neufahrn. The apparatus measures the distribution of the toner particles charge (in fC) with respect to a measured toner particle diameter (diameter in 10µm). The measurement results are expressed as a percentage particle frequency of the same q/d ratio (y-axis) on q/d ratio expressed as fC/10µm (in x-axis). From those data the mean q/d value can be calculated

Melt viscosity of toner particles

[0055] The melt viscosity is measured in a CSL2 500 Carr-Med Rheometer from TA Instruments at 120°C. The viscosity measurement is carried out at a sample temperature of 120°C. The sample having a weight of 0.75 g is applied in the measuring gap (about 1.5 mm) between two parallel plates of 20 mm diameter one of which is oscillating about its vertical axis at 6 rad/sec and amplitude of 10⁻³ radians. The sample is temperature equilibrated for 10 min at 120°C. measuring gap (about 1.5 mm) between two parallel plates of 20 mm diameter one of which is oscillating about its vertical axis at 6 rad/sec and amplitude of 10⁻³ radians. The sample is temperature equilibrated for 10 min at 120°C.

Temperature resistance test of fused and cured toner particles

[0056] The fused and cured samples are folded inside and put between 2 plates for 5 sec with a pressure of 6 bar. Only the upper plate is heated. The temperature at which the toner starts to stick together is determined for the uncured and corresponding cured toner sample. The temperature difference between both toner samples is a measure for the temperature resistance of the toner.

Images defects after temperature resistance test

[0057] After the temperature resistance test the images are visually observed and ranked on a scale:
1=excellent: no damage could be seen
5=bad: severe damage of the toner image (by the melting of the toner during the temperature exposure)

Solvent resistance test of fused and cured toner particles

[0058] With a cloth soaked with MEK (methylethylketone) the fused and cured toner images are rubbed softly. One count is equal to an up and down rub. The rubs are counted till the substrate becomes visible. The number of rubs is a measure for the solvent resistance of the toner images
Abrasion resistance of fused and cured toner particles

[0059] The toner images with an area of 16cm² are rubbed 50 times with a load of 600g by an abrasion paper on an abrasion tester type Prüfbau from Dr Durner in München. The abrasion paper is a sand paper P600 which is rubbed 10 x over each other in the same apparatus.

[0060] Afterwards the uncured and corresponding cured images are visually inspected and the difference between both samples is ranked as follows:

1=excellent: cured samples are much better than uncured samples- no damage of the image, only a small lowering in gloss
3= good/acceptable: cured samples are better than uncured samples : small damage of the image and significant lowering in gloss
5=bad: cured samples are equal to uncured samples: strong damage of the image.

Tg of toner particles and resin

[0061] The glass transition temperature is preferably determined in accordance with ASTM D3418-82.

EXAMPLES

[0062] Table 1:

<table>
<thead>
<tr>
<th>polymers</th>
<th>composition</th>
<th>Tg</th>
<th>Tm</th>
</tr>
</thead>
<tbody>
<tr>
<td>UV1</td>
<td>unsaturated polyester (terephthalic acid/neopentylglycol polyester)</td>
<td>51</td>
<td></td>
</tr>
<tr>
<td>UV2</td>
<td>unsaturated polyester (terephthalic acid/neopentylglycol polyester)</td>
<td>46</td>
<td></td>
</tr>
<tr>
<td>PE1</td>
<td>terephthalic acid /isophalic acid dianol 33</td>
<td>53</td>
<td>95</td>
</tr>
<tr>
<td>PE2</td>
<td>terephthalic acid /isophalic acid dianol 22/dianol 33</td>
<td>60</td>
<td>105</td>
</tr>
<tr>
<td>PE3</td>
<td>terephthalic acid /isophalic acid dianol 22/dianol 33</td>
<td>71</td>
<td>140</td>
</tr>
</tbody>
</table>

Example 1 (embodiment of the present invention)

[0063] 94 parts of resin UV1, 3 parts of Cu-phtalocyanine, 1.5 parts photoinitiator type Irgacure 651 (from Ciba Geigy) and 1.5 parts photoinitiator type Irgacure 819 (from Ciba Geigy) were meltblended for 30 minutes in a laboratory kneader at 110°C. After cooling, the solidified mass was pulverized and milled using a Alpine fliessbettgegenstrahlmuhle 100AFG (trade name) and further classified using a multiplex zig-zag classifier type 100MZR (trade name).

[0064] The average particle size of the toner particles was measured by a coulter counter model multisizer and was found to be 8.4 μm by volume.

[0065] In order to improve the flowability of the toner particles, the particles were mixed with 0.5% of hydrophobic colloidal silica type R972 (trade name) from Degussa.

Example 2 (embodiment of the present invention)

[0066] 92.5 parts of resin UV1, 3 parts of Cu-phtalocyanine, 2.25 parts photoinitiator type Irgacure 651 (from Ciba Geigy) and 2.25 parts photoinitiator type Irgacure 819 (from Ciba Geigy) were meltblended for 30 minutes in a laboratory kneader at 110°C. After cooling, the solidified mass was pulverized and milled using a Alpine fliessbettgegenstrahlmuhle 100AFG (trade name) and further classified using a multiplex zig-zag classifier type 100MZR (trade name).

[0067] The average particle size of the toner particles was measured by a coulter counter model multisizer and was found to be 8.6 μm by volume.

[0068] In order to improve the flowability of the toner particles, the particles were mixed with 0.5% of hydrophobic colloidal silica type R972 (trade name) from Degussa.
Example 3 (embodiment of the present invention)

[0069] 94 parts of resin UV1, 3 parts of Cu-phthalocyanine, 0.75 parts photoinitiator type Irgacure 651 (from Ciba Geigy) and 2.25 parts photoinitiator type Irgacure 819 (from Ciba Geigy) were meltblended for 30 minutes in a laboratory kneader at 110°C. After cooling, the solidified mass was pulverized and milled using a Alpine fliessbettgegenstrahlmuhle 100AFG (trade name) and further classified using a multiplex zig-zag classifier type 100MZR (trade name).

[0070] The average particle size of the toner particles was measured by a coulter counter model multisizer and was found to be 8.3 \(\mu\text{m}\) by volume.

[0071] In order to improve the flowability of the toner particles, the particles were mixed with 0.5% of hydrophobic colloidal silica type R972 (trade name) from Degussa.

Example 4 (embodiment of the present invention)

[0072] 94 parts of resin UV1, 3 parts of Cu-phthalocyanine, 2.25 parts photoinitiator type Irgacure 651 (from Ciba Geigy) and 0.75 parts photoinitiator type Irgacure 819 (from Ciba Geigy) were meltblended for 30 minutes in a laboratory kneader at 110°C. After cooling, the solidified mass was pulverized and milled using a Alpine fliessbettgegenstrahlmuhle 100AFG (trade name) and further classified using a multiplex zig-zag classifier type 100MZR (trade name).

[0073] The average particle size of the toner particles was measured by a coulter counter model multisizer and was found to be 8.9 \(\mu\text{m}\) by volume.

[0074] In order to improve the flowability of the toner particles, the particles were mixed with 0.5% of hydrophobic colloidal silica type R972 (trade name) from Degussa.

Example 6 (embodiment of the present invention)

[0077] 66 parts of resin UV1, 25 parts of resin PE1, 3.4 parts magenta pigment PR 122, 2.6 parts magenta pigment PR181, 1.5 parts photoinitiator type Irgacure 651 (from Ciba Geigy) and 1.5 parts photoinitiator type Irgacure 819 (from Ciba Geigy) were meltblended for 30 minutes in a laboratory kneader at 110°C. After cooling, the solidified mass was pulverized and milled using a Alpine fliessbettgegenstrahlmuhle 100AFG (trade name) and further classified using a multiplex zig-zag classifier type 100MZR (trade name).

[0078] The average particle size of the toner particles was measured by a coulter counter model multisizer and was found to be 8.8 \(\mu\text{m}\) by volume.

Example 7 (embodiment of the present invention)

[0080] 91.5 parts of resin UV1, 4 parts parts of pigment yellow PY 185, 1.12 parts photoinitiator type Irgacure 651 (from Ciba Geigy) and 3.36 parts photoinitiator type Irgacure 819 (from Ciba Geigy) were meltblended for 30 minutes in a laboratory kneader at 110°C. After cooling, the solidified mass was pulverized and milled using a Alpine fliessbettgegenstrahlmuhle 100AFG (trade name) and further classified using a multiplex zig-zag classifier type 100MZR (trade name).

[0081] The average particle size of the toner particles was measured by a coulter counter model multisizer and was found to be 8.5 \(\mu\text{m}\) by volume. Alpine fliessbettgegenstrahlmuhle 100AFG (trade name) and further classified using a multiplex zig-zag classifier type 100MZR (trade name).

[0082] The average particle size of the toner particles was measured by a coulter counter model multisizer and was found to be 8.5 \(\mu\text{m}\) by volume.

[0083] In order to improve the flowability of the toner particles, the particles were mixed with 0.5% of hydrophobic colloidal silica type R972 (trade name) from Degussa.
Example 8 (embodiment of the present invention)

92.5 parts of resin UV1, 6 parts carbon black (cabot regal 400 from Cabot Corporation), 1.5 parts photoinitiator type Irgacure 651 (from Ciba Geigy) and 1.5 parts photoinitiator type Irgacure 819 (from Ciba Geigy) were meltblended for 30 minutes in a laboratory kneader at 110°C. After cooling, the solidified mass was pulverized and milled using a Alpine fliessbettgegenstrahlmuhle 100AFG (trade name) and further classified using a multiplex zig-zag classifier type 100MZR (trade name).

The average particle size of the toner particles was measured by coulter counter model multisizer and was found to be 8.2 µm by volume.

In order to improve the flowability of the toner particles, the particles were mixed with 0.5% of hydrophobic colloidal silica type R972 (trade name) from Degussa.

Example 9 (embodiment of the present invention)

93 parts of resin UV1, 3 parts of Cu-phtalocyanine, 1 parts of CCA type Copycharge N4P (trade name) from Clariant GmbH, 1.5 parts photoinitiator type Irgacure 651 (from Ciba Geigy) and 1.5 parts photoinitiator type Irgacure 819 (from Ciba Geigy) were meltblended for 30 minutes in a laboratory kneader at 110°C. After cooling, the solidified mass was pulverized and milled using a Alpine fliessbettgegenstrahlmuhle 100AFG (trade name) and further classified using a multiplex zig-zag classifier type 100MZR (trade name).

The average particle size of the toner particles was measured by coulter counter model multisizer and was found to be 8.4 µm by volume.

In order to improve the flowability of the toner particles, the particles were mixed with 0.5% of hydrophobic colloidal silica type R972 (trade name) from Degussa.

Example 10 (embodiment of the present comparative)

97 parts of resin PE2, and 3 parts of were meltblended for 30 minutes in a laboratory kneader at 110°C. After cooling, the solidified mass was pulverized and milled using a Alpine fliessbettgegenstrahlmuhle 100AFG (trade name) and further classified using a multiplex zig-zag classifier type 100MZR (trade name).

The average particle size of the toner particles was measured by coulter counter model multisizer and was found to be 8.1 µm by volume.

In order to improve the flowability of the toner particles, the particles were mixed with 0.5% of hydrophobic colloidal silica type R972 (trade name) from Degussa.

Example 11 (comparative)

97 parts of resin PE3 and 3 parts of Cu-phtalocyanine were meltblended for 30 minutes in a laboratory kneader at 110°C. After cooling, the solidified mass was pulverized and milled using a Alpine fliessbettgegenstrahlmuhle 100AFG (trade name) and further classified using a multiplex zig-zag classifier type 100MZR (trade name).

The average particle size of the toner particles was measured by coulter counter model multisizer and was found to be 8.5 µm by volume.

In order to improve the flowability of the toner particles, the particles were mixed with 0.5% of hydrophobic colloidal silica type R972 (trade name) from Degussa.

Example 12 (comparative)

97 parts of resin UV1, 1.5 parts photoinitiator type Irgacure 651 (from Ciba Geigy) and 1.5 parts photoinitiator type Irgacure 819 (from Ciba Geigy) were meltblended for 30 minutes in a laboratory kneader at 110°C. After cooling, the solidified mass was pulverized and milled using a Alpine fliessbettgegenstrahlmuhle 100AFG (trade name) and further classified using a multiplex zig-zag classifier type 100MZR (trade name).

The average particle size of the toner particles was measured by coulter counter model multisizer and was found to be 8.45 µm by volume.

In order to improve the flowability of the toner particles, the particles were mixed with 0.5% of hydrophobic colloidal silica type R972 (trade name) from Degussa.

Example 13 (comparative)

92.5 parts of resin UV2, 3 parts of Cu-phtalocyanine, 2.25 parts photoinitiator type Irgacure 651 (from Ciba
Geigy) and 2.25 parts photoinitiator type Irgacure 819 (from Ciba Geigy) were meltblended for 30 minutes in a laboratory kneader at 110°C. After cooling, the solidified mass was pulverized and milled using an Alpine fliessbettgegenstrahlmühle 100AFG (trade name) and further classified using a multiplex zig-zag classifier type 100MZR (trade name).

[0100] The average particle size of the toner particles was measured by coulter counter model multisizer and was found to be 8.4 µm by volume.

In order to improve the flowability of the toner particles, the particles were mixed with 0.5% of hydrophobic colloidal silica type R972 (trade name) from Degussa.

Developers

[0101] With the toners from example 1, 3 and 4, developers were prepared by mixing 5g of said toner particles together with 100g of a 0.5%w/w coated silicone MnMgSr ferrite carrier with a dv50 of 45µm.

[0102] Images were developed on an uncoated paper of 135g/m2 and PET foil of 100 µm with an applied mass of 0.5, 1 and 1.5 mg/cm2 corresponding to 1, 2 and 3 toner layers.

[0103] With the toners from example 2, 5, 6, 7, 8, 9, 10 and 11 developers were prepared by mixing 5g of said toner particles together with 100g of a 0.5%w/w coated silicone CuZn ferrite carrier with a dv50 of 55µm.

[0104] Images were developed on an uncoated paper of 135 g/m2 with an applied mass of 0.5, 1 and 1.5 mg/cm2 corresponding to 1, 2 and 3 toner layers.

[0105] Using toner 12, a developer was prepared in the same manner as with toner 2. With this developer a clear UV toner was applied in an amount of 0.5mg/cm2 on top of an image of 1mg/cm2 based on toner 10.

[0106] With toner 13 also a developer was prepared in the same manner as with toner 2. After activating the developer in the developing unit, a lot of toner lumps were observed due to the low Tg of the toner meaning that no high quality images could be made. The toner images were fused and UV cured inline as mentioned in table 2. Example 2 was also cured offline. The same results were found as for the online curing of the toner images. The results are shown in table 2.
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Table 2: test results: Notes:

(1) temperature at which the toner sticks together according to the temperature resistance test

(2) difference in temperature, at which the fused toner sticks together, between the cured and corresponding uncured sample

(3) Gallium doped Hg-lamp

(4) the solvent resistance of the corresponding uncured toner image of examples 1 to 9 is 1 rub

It is clear from these results that there is in some cases a large difference in temperature resistance between cured and non-cured samples. The temperature of toner sticking can be slightly improved with the use of a higher Tg-resin
but it never reached the desired levels obtained with UV-curable pigmented toners. With a clear coat based on curable
toner particles the temperature of toner sticking can be greatly improved but image defects are observed in the under-
lying uncured pigmented toner layers. It is also clear that the dose and the curing speed have to be adjusted in order
to obtain the desired increase in temperature resistance of at least 50°C. It is also clear that a toner with a Tg lower
than 40°C is not very suitable.

Claims

1. Dry toner particles comprising:
   at least a UV curable resin, and
   a coloring agent, wherein:
   - the UV curable resin has a Tg > 45°C
   - the toner particles comprising the radiation curable resin have a Tg > 40°C,
   - the temperature resistance of the toner particles when fused and cured is larger than 50°C,
   - the particle size of the toner particles is between 4 and 14µm.

2. Dry toner particles according to claim 1, further comprising a photoiniator.

3. Dry toner particles according to claim 1 or 2 wherein said UV curable resin is a polyester resin.

4. Dry toner particles according to any previous claim, wherein the temperature resistance of the fused and cured
toner particles is larger than >80°C.

5. Dry toner particles according to any of the claims 1 to 4, wherein the particle size of the toner particles is between
5 and 10µm.

6. Dry toner particles according to any of the claims 1 to 5, wherein the viscosity of the toner particles is between
100 and 1500 Pa.s.

7. Dry toner particles according to any of the claims 1 to 6, wherein the solvent resistance of the fused and cured
toner particles > 7 MEK rubs.

8. Dry toner particles according to any previous claim, wherein the abrasion resistance of the fused and cured toner
particles is lower or equal to 3.

9. Dry electrostatographic developer composition comprising carrier particles and toner particles according to any of
the claims 1 to 8 and wherein
   - the carrier particles have a volume average particle size of between 30 to 65µm,
   - said carrier particles comprise a core particle coated with a resin in an amount of 0.4 to 2.5%,
   - the absolute charge expressed as fC/10µm (q/d) is between 3 and 13 fC/10µm.

10. A method of fusing and curing dry toner particles according to any of claims 1 to 8, comprising:
   - selectively imagewise depositing radiation curable toner particles on a substrate to form an image comprising
     areas of deposited toner and areas of no deposited toner,
   - fusing the toner particles on the substrate, and
   - radiation curing the fused toner.

11. A method according to claim 10 wherein the fusing and curing is done in-line.

12. A method according to claim 10 or 11 wherein the radiation curing is with UV light.

13. A method according to claim 12, wherein the UV dose is between 3 and 30 J/cm2.
14. A method according to any of the claims 10 to 13 wherein the substrate is a polymeric or plastic foil.

15. A substrate printed with a toner comprising the toner particles of any of claims 1 to 8.
### DOCUMENTS CONSIDERED TO BE RELEVANT

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**TECHNICAL FIELDS SEARCHED (Int.Cl.7)**

- G03G
- D21H

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- A: technological background
- C: non-written disclosure
- D: document cited in the application
- L: document cited for other reasons
- T: member of the same patent family, corresponding document
## DOCUMENTS CONSIDERED TO BE RELEVANT

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**Date of completion of the search**: 9 May 2003  
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ANNEX TO THE EUROPEAN SEARCH REPORT
ON EUROPEAN PATENT APPLICATION NO. EP 03 44 7003

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For more details about this annex: see Official Journal of the European Patent Office, No. 12/82