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(71) Applicant:
SAMSUNG ELECTRONICS CO., LTD.
Suwon-City, Kyungki-do (KR)

(72) Inventors:
- **Park, Moon-soo**
  Dongjak-gu, Seoul (KR)
- **Hong, Soon-kil**
  Suwon-city, Kyungki-do (KR)
- **Noh, Jin-young**
  Kwangmyung-city, Kyungki-do (KR)

(74) Representative:
Chugg, David John
Appleyard Lees,
15 Clare Road
Halifax, West Yorkshire HX1 2HY (GB)

(54) Toner composition and method of preparing toner using the same

(57) A toner composition and a method of preparing toner particles using the toner composition. The toner composition comprises a monomer for a binding resin, a colouring agent, a stabilizer, a charge controller, a lubricant and a polymerization initiator, wherein the stabilizer is obtained by dispersing hydrophobic silica into distilled water of pH 10~14, and then adjusting pH of the dispersion into 6~8. The toner particles prepared from the toner composition have improved in charge quantity, average particle diameter and distribution in particle diameter. Particularly, when the toner composition contains a surfactant, dispersion property of the colour agent and the charge controller can be improved, thereby resulting in a better image quantity.

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Description

[0001] The present invention relates to a toner composition and a method of preparing toner using the same, and more particularly, to a toner composition having improved particle diameter and charge quantity characteristics of toner as well as improved dispersion property of a colouring agent, and a method of preparing toner using the toner composition.

[0002] Recently, demand for printers has gradually increased with development in computer industries. Accordingly, the amount of toner used has also increased.

[0003] Toner particles used for displaying an image are generally prepared by a grinding method. According to the grinding method, a polymer bonding resin, a colouring agent and a charge controller, etc. are blended in a dry condition. Then, the mixture is melt-mixed and cooled. The resultant is ground to fine toner particles.

[0004] Toner particles prepared by the above method have a wide distribution of particle diameters. Because toner particles outside a predetermined diameter range must be excluded, it is an economically unfavourable method. Limitation in dispersion of the charge controller and the colouring agent, and the shape of the toner particles often leads to an unsatisfactory resolution. To solve these problems, spherical toner particles have been prepared by polymerization technique.

[0005] This polymerization technique is classified into an emulsion polymerization method and a suspension polymerization method. According to the emulsion polymerization method, the final toner particle is usually smaller than 5μm in diameter. It, however, causes an adverse effect on human body. As a result, it would be is difficult to use these particles in preferred printers. This is why the suspension polymerization method is a preferred polymerization method.

[0006] A method of preparing toner by the suspension polymerization method is described as follows.

[0007] Water is used as a reaction medium, and a monomer for a binding resin, a charge controller, a stabilizer, a lubricant and a colouring agent are added to the reaction medium, and then polymerization is performed.

[0008] After the polymerization is completed, spherical particles sediment inside the reaction mixture. The obtained particles are filtered and then dried, producing the toner particles.

[0009] Phosphate or hydrophobic silica is used as the stabilizer. When using phosphate as the stabilizer, however, the particle diameter of the final toner particles tends to be very large, i.e., over approximately 35μm, and the particle diameter distribution shows a wide variation ranging from a few to hundred micrometers in diameter. These particles contributes to lowering charge characteristics, and thus not have proper properties as toner.

[0010] On the other hand, when the hydrophobic silica is used as the stabilizer, it is very difficult for the silica to be dispersed into the water. As a result, the polymerization reaction cannot occur. Therefore, the hydrophobic silica must be solubilized in an organic solvent, such as methanol, before it could be miscible with the other constituents of the toner composition for the polymerization.

[0011] To solve the above problems, it is an aim of preferred embodiments of the present invention to provide a toner composition which has improved particle diameter characteristics of toner particles and dispersion properties of filler particles, such as a charge controller and a colouring agent.

[0012] It is another aim of preferred embodiments of the present invention to provide a method of preparing toner using the composition.

[0013] According to a first aspect of the invention, there is provided a toner composition comprising a monomer for a binding resin, a colouring agent, a stabilizer, a charge controller, a lubricant and a polymerization initiator, wherein the stabilizer is obtained by dispersing hydrophobic silica into distilled water of pH 10~14, and then adjusting the pH of the dispersion into the range 6~8.

[0014] Preferably, the mixing ratio of the monomer for a binding resin and the silica solid content is between 50:1 and 25:1 by weight.

[0015] The toner composition may further comprise an ionic surfactant.

[0016] The mixing ratio of the monomer for binding resin and the ionic surfactant is preferably between 1000:1 and 2000:1 by weight.

[0017] The ionic surfactant is preferably selected from the group consisting of sodium lauryl sulfate, cetyltrimethylammonium bromide and cetyltrimethylammonium chloride.

[0018] According to a second aspect of the invention, there is provided a method of preparing a toner composition comprising the steps of:

(a) adjusting the pH of distilled water to pH 10~14 with an aqueous base, and dispersing hydrophilic silica into the pH-adjusted distilled water;

(b) adjusting the pH of the mixture of the step (a) to pH 6~8;

(C) mixing a monomer for a binding resin, a polymerization initiator, a charge controller, a lubricant and a colouring agent, and adding the mixture to the resultant of the step (b);

(d) preparing toner particles by polymerizing the resultant of the step (c); and

(e) removing foreign materials remaining on the surface of toner particles.

[0019] By "distilled water" we mean any water of high purity, including demineralised or de-ionised water, or any other purified grad of water.

[0020] Preferably, the aqueous base is selected from the group consisting of ammonium hydroxide, sodium hydroxide and potassium hydroxide.

[0021] The mixing ratio of the monomer for a binding resin and the silica solid content is preferably between 50:1 and 25:1 by weight.

[0022] In the step (c) of mixing the monomer for a binding resin, the polymerization initiator, the charge controller, the lubricant and the colouring agent, an ionic surfactant is preferably further added.

[0023] Preferably, the ionic surfactant is selected from the group consisting of sodium lauryl sulfate, cetyltrimethylammonium bromide and cetyltrimethylammonium chloride.

[0024] The mixing ratio of the monomer for binding resin and the ionic surfactant is preferably between 1000:1 and 2000:1 by weight.

[0025] For a better understanding of the invention, and to show how embodiments of the same may be carried into effect, reference will now be made, by way of example, to the accompanying diagrammatic drawings, in which:

Figures 1 through 7 show representations of optical microscope photographs of toner particles prepared by Examples 1 through 5 according to embodiments of the present invention and Comparative Examples 3 and 4; and

Figures 8 through 14 are diagrams showing distribution of particle diameter of toner particles prepared by Examples 1 through 5 according to the embodiments of the present invention and Comparative Examples 3 and 4.

[0026] A toner composition of an embodiment of the present invention is characterized by a stabilizer which is obtained by dissolving hydrophobic silica in distilled water of pH 10~14, and then neutralizing the resultant to pH 6~8. When thus-obtained stabilizer is mixed with a monomer for a binding resin, a colouring agent, a charge controller, a lubricant and a polymerization initiator, a uniformly dispersed toner composition can be obtained unlike the conventional toner composition.

[0027] Preferably, the mixing ratio of the monomer for a binding resin and the silica solid content is between 50:1 and 25:1 by weight. Here, if the mixing content of the silica solid is over the above range, it is very difficult to recover toner particles after polymerization. Also, if the mixing content of the silica solid is less than the above range, toner particles agglomerate unfavourably.

[0028] Also, the toner composition may further comprise an ionic surfactant. Here, the ionic surfactant may be an anionic or cationic surfactant without restriction.

[0029] As the anionic surfactant, sodium lauryl sulfate is suitably used. The cationic surfactant may be cetyltrimethylammonium bromide or cetyltrimethylammonium chloride. Also, preferably, the mixing ratio between the monomer for a binding resin and the surfactant is in the range of 1000:1~2000:1 by weight. Here, if the mixing content of the surfactant exceeds the above range, it is difficult to recover toner particles. On the other hand, if the mixing content of the surfactant is less than the above range, dispersion properties of filler particles become poor.

[0030] The monomer for a binding resin includes any monomers generally used when preparing toner particles by polymerization. In the present invention, a combination of styrene and butylmethacrylate is preferably used. Here, the mixing ratio of styrene and butylmethacrylate is suitably 6:4~9:1 based on weight, preferably 7:3~8:2.

[0031] The charge controller controls the charging properties of the toner, and includes any general charge controllers without limitations. Also, the colouring agent is suitably carbon black as a black pigment.

[0032] The lubricant improves fluidity of toner particles. Here, wax is suitably used for this purpose. Also, the polymerization initiator may be any general polymerization initiator.

[0033] Hereinafter, a method of preparing toner particles using the toner composition will be described.

[0034] After adjusting the pH of distilled water to 10~14 using an aqueous base, hydrophobic silica is dispersed into the pH-adjusted distilled water. Then, the mixture is neutralized to pH 6~8. Here, the aqueous base may be sodium hydroxide, potassium hydroxide or ammonium hydroxide without limitation. Also, so as to neutralize the hydrophobic silica dispersion of pH 10-14, any acid may be used without restriction. However, formic acid is preferred.

[0035] A mixture of a monomer for a binding resin, a charge controller, a colouring agent, a lubricant and a polymerization initiator is added to the resultant, and then uniformly mixed. If required, an ionic surfactant, preferably, an cationic surfactant, may be further added to the mixture. This mixing process is preferably performed by a ball mill.

[0036] Then, polymerization is performed on the resultant under an inert atmosphere, for example nitrogen. After the polymerization is completed, unreacted residues are removed from the reaction mixture using methanol. Here, if a conversion ratio of the polymerization reaction reaches as low as 70~80%, then methanol is preferably used to remove the unreacted residues. On the other hand, if the conversion is found to be as high as 80% or over, the unreacted residues are preferably removed using distilled water.

[0037] Then, the obtained precipitate is filtered, and foreign materials remaining on the surface of the precipitate are removed using a dilute potassium hydroxide aqueous solution or methanol. The resultant mass from which the foreign materials were removed is dried in a vacuum oven for a predetermined time, thereby resulting in toner particles of the present invention.

[0038] The average diameter of the toner particles obtained by the above method is 5~20μm, the charge quantity is -10~-20μc/g, and the glass transition temperature is 60~75°C.

[0039] Hereinafter, embodiments of the present invention will be described through the following examples. However, the present invention is not limited to the following examples.

〈Example 1〉

[0040] Ammonium hydroxide aqueous solution was added to 600ml of distilled water to adjust the pH to approximately 10, and then 6g of hydrophobic silica S-972 (Degussa Co.) was added to the pH-adjusted distilled water. Then, the resultant was stirred using a homogenizer at 5,000rpm for 10 minutes. Then, the resultant was neutralized using formic acid to prepare a first composition.

[0041] 140ml of styrene, 60ml of butylmethacrylate, 4g of 2,2-azobisisobutyronitrile, 6g of Carbon black 2350 (Mitsubishi Co., average diameter: 15nm), 2g of Bontron S-34 (Orient Chemical Co.) and 2g of wax were mixed to prepare a second composition.

[0042] The mixture of the first composition and the second composition was stirred in a ball-mill for 12 hours. Then, the polymerization was performed at 75°C for 7 hours under a nitrogen atmosphere.

[0043] After the polymerization was completed, unreacted styrene and butylmethacrylate were removed from the reaction mixture using methanol. Then, the resultant was filtered and cleaned, and dried in a vacuum oven for 2 days, resulting in toner particles.

〈Example 2〉

[0044] Toner particles were prepared by the same method as Example 1, except that the carbon black content was 10g.

〈Example 3〉

[0045] Toner particles were prepared by the same method as Example 1, except that 0.1g of cetyltrimethylammonium bromide (CTAB) was additionally included in the first composition.

〈Example 4〉

[0046] Toner particles were prepared by the same method as Example 1, except that sodium hydroxide solution was used to prepare an alkaline hydrophobic silica solution, instead of ammonium hydroxide aqueous solution.

〈Example 5〉

[0047] Toner particles were prepared by the same method as Example 1, except that Printex L-6 (Degussa Co, average diameter: 18nm) was used as carbon black, instead of Carbon black 2350 (Mitsubishi Co.).

〈Comparative Example 1〉

[0048] 400ml of distilled water and 100ml of methanol were mixed, and then 6g of hydrophobic silica R-972 (Degussa Co.) was dispersed into the mixture, to prepare a first composition.

[0049] 140ml of styrene and 60ml of butylmethacrylate were mixed with 600ml of distilled water, and then 4g of 2,2-azobisisobutyronitrile, 6g of carbon black, 2g of Bontron S-34 and 2g of wax were added to the mixture, to prepare a second composition.

[0050] After adding the second composition to the first composition, the polymerization was performed on the reaction mixture at 75°C for 7 hours under a nitrogen atmosphere.

[0051] After the reaction was completed, unreacted styrene and butylmethacrylate were removed from the reaction mixture using methanol. Then, the resultant was filtered and cleaned, and then dried in a vacuum oven for 2 days, resulting in toner particles.

〈Comparative Example 2〉

[0052] Toner particles were prepared by the same method as Example 1, except that di-n-butylamine was used to prepare the first composition instead of ammonium hydroxide aqueous solution.

〈Comparative Example 3〉

[0053] 3g of tri-calcium phosphate ($Ca_3(PO_4)_2$, Yakuri Pure Chemicals) was added to 600ml of distilled water, to prepare a first composition.

[0054] 140ml of styrene, 60ml of butylmethacrylate, 2g of 2,2-azobisisobutyronitrile, 6g of Carbon black 2350 (Mitsubishi Co., average diameter: 15nm), 2g of Bontron S-34 (Orient Chemical Co.) and 2g of wax were mixed to prepare a second composition.

[0055] After adding the second composition to the first composition, the mixture was stirred in a ball-mill for 12 hours. Then, the polymerization was performed at 75°C for 7 hours under a nitrogen atmosphere.

[0056] After the reaction was completed, unreacted styrene and butylmethacrylate were removed from the reaction mixture using methanol. Then, the resultant was filtered and cleaned, and dried in a vacuum oven for 2 days, resulting in toner particles.

〈Comparative Example 4〉

[0057] Toner particles were prepared by the same method as Example 1, except that the first composition and the second composition were mixed in a homogenizer.

[0058] According to Comparative Example 1, the conversion of the polymerization reaction was very low, and it was difficult to obtain spherical toner particles after the polymerization. Also, in the case when the first composition was prepared by using n-butyl alcohol (Comparative Example 2), the hydrophobic silica agglomerated, such that it was difficult to obtain a uniform first composition. Thus, the polymerization reaction to form the toner particles cold not be conducted.

[0059] Characteristics of the toner particles prepared by the Examples 1-5 and Comparative Examples 3-4 was evaluated as follows.

[0060] Particle diameters of the toner particles and particle diameter distribution were measured by a coulter counter or a laser particle diameter analyzer, and the surface of the toner particles was analyzed with a scanning electron microscope (SEM).

[0061] Dispersion properties of carbon black in the toner particles were evaluated with an optical microscope (Labophot-2, Nicon Co.), and represented as follows:

◎ : carbon black is very finely dispersed;
○ : carbon black is finely dispersed;
△ : large particles of carbon black are slightly visible; and
X : large particles of carbon black are clearly visible.

[0062] The glass transition temperature was measured by using a differential scanning calorimeter (DSC), and the molecular weight was measured with a gel permeation chromatography (GPC).

[0063] The charge quantity of toner particles was measured by using a blow-off meter (Toshiba Co.).

[0064] On the other hand, the toner particles prepared by the Examples 1-5 and Comparative Examples 3-4 were measured to analyze the dispersion state of the carbon black, the average particle diameter, the glass transition temperature and the charge quantity. Their results are tabulated in Table 1.

Table 1

classification	dispersion state of carbon black	average particle diameter (μm)	glass transition temperature (°C)	charge quantity (μc/g)
Example 1	○	12.57	68.04	-11.54

Table 1 (continued)

classification	dispersion state of carbon black	average particle diameter (μm)	glass transition temperature (°C)	charge quantity (μc/g)
Example 2	○	13.76	66.14	-12.16
Example 3	◎	12.87	64.37	-15.48
Example 4	◎	12.75	67.48	-12.16
Example 5	◎	5.25	66.22	-20.27
Comparative Example 3	△	38.28	65.36	+7.35
Comparative Example 4	△	26.99	66.12	-9.56

[0065] As can be seen from Table 1, the toner particles prepared by Examples 1-5 have excellent degree of dispersion compared with Comparative Examples 3 and 4.

[0066] Particularly, the diameter of the toner particles prepared by Comparative Example 3 tends to be divided into two classes, i.e., 20μm or more and 10μm or less. In this case, pigments are dispersed to some extent within the toner particles having 20μm or more in diameter while the pigment cannot be incorporated into the toner particles having 10μm or less in diameter.

[0067] Figures 1 through 5 are optical microscope photographs of the toner particles prepared by Examples 1 through 5, and Figures 6 and 7 are optical microscope photographs of the toner particles prepared by Comparative Examples 3 and 4.

[0068] Referring to Figures 1 through 5, it can be seen that the toner particles of Examples 1 through 5 have excellent degree of dispersion of the carbon black compared with Comparative Examples 3 and 4. In Particular, referring to Figure 3, in the case when cetyltrimethylammonium bromide (CTAB) is additionally added (Example 3), the carbon black is evenly dispersed into the toner particles.

[0069] Particle distribution of the toner particles prepared by Examples 1-5 and Comparative Examples 3 and 4 are shown in Figures 8 through 14.

[0070] Referring to Figures 8 through 14, the distribution characteristics in particle diameter of the toner particles is improved in Examples 1 through 5, compared with Comparative Examples 3 and 4.

[0071] Also, as can be seen from Table 1, the toner particles prepared by Examples 1-5 show improvement in the charge quantity and the average particle diameter, compared with Comparative Examples 3 and 4.

[0072] Toner particles having improved in charge quantity, average particle diameter and particle diameter distribution can be prepared from the toner composition of embodiments of the present invention. Particularly, when the toner composition contains a surfactant, toner particles exhibiting improved dispersion properties of the colouring agent and charge controller can be obtained, thereby resulting in a better image quality.

[0073] The reader's attention is directed to all papers and documents which are filed concurrently with or previous to this specification in connection with this application and which are open to public inspection with this specification, and the contents of all such papers and documents are incorporated herein by reference.

[0074] All of the features disclosed in this specification (including any accompanying claims, abstract and drawings), and/or all of the steps of any method or process so disclosed, may be combined in any combination, except combinations where at least some of such features and/or steps are mutually exclusive.

[0075] Each feature disclosed in this specification (including any accompanying claims, abstract and drawings), may be replaced by alternative features serving the same, equivalent or similar purpose, unless expressly stated otherwise. Thus, unless expressly stated otherwise, each feature disclosed is one example only of a generic series of equivalent or similar features.

[0076] The invention is not restricted to the details of the foregoing embodiment(s). The invention extends to any novel one, or any novel combination, of the features disclosed in this specification (including any accompanying claims, abstract and drawings), or to any novel one, or any novel combination, of the steps of any method or process so disclosed.

Claims

1. A toner composition comprising a monomer for a binding resin, a colouring agent, a stabilizer, a charge controller, a lubricant and a polymerization initiator,

   wherein the stabilizer is obtained by dispersing hydrophobic silica into distilled water of pH 10~14, and then adjusting pH of the dispersion into 6~8.

2. The toner composition of claim 1, wherein the mixing ratio of the monomer for a binding resin and the silica solid content is between 50:1 and 25:1 by weight.

3. The toner composition of claim 1, further comprising an ionic surfactant.

4. The toner composition of claim 3, wherein the mixing ratio of the monomer for binding resin and the ionic surfactant is between 1000:1 and 2000:1 by weight.

5. The toner composition of claim 3, wherein the ionic surfactant is selected from the group consisting of sodium lauryl sulfate, cetyltrimethylammonium bromide and cetyltrimethylammonium chloride.

6. A method of preparing a toner composition comprising the steps of:

(a) adjusting the pH of distilled water to pH 10~14 with an aqueous base, and dispersing hydrophilic silica into the pH-adjusted distilled water;

(b) adjusting the pH of the mixture of the step (a) to pH 6~8;

(c) mixing a monomer for a binding resin, a polymerization initiator, a charge controller, a lubricant and a colouring agent, and adding the mixture to the resultant of the step (b);

(d) preparing toner particles by polymerizing the resultant of the step (c); and

(e) removing foreign materials remaining on the surface of the toner particles.

7. The method of claim 6, wherein the aqueous base is selected from the group consisting of ammonium hydroxide, sodium hydroxide and potassium hydroxide.

8. The method of claim 6, wherein the mixing ratio of the monomer for a binding resin and the silica solid content is between 50:1 and 25:1 by weight.

9. The method of claim 6, wherein in the step (c) of mixing the monomer for a binding resin, the polymerization initiator, the charge controller, the lubricant and the colouring agent, an ionic surfactant is further added.

10. The method of claim 9, wherein the ionic surfactant is selected from the group consisting of sodium lauryl sulfate, cetyltrimethylammonium bromide and cetyltrimethylammonium chloride.

11. The method of claim 9, wherein the mixing ratio of the monomer for binding resin and the ionic surfactant is between 1000:1 and 2000:1 by weight.

FIG. 1

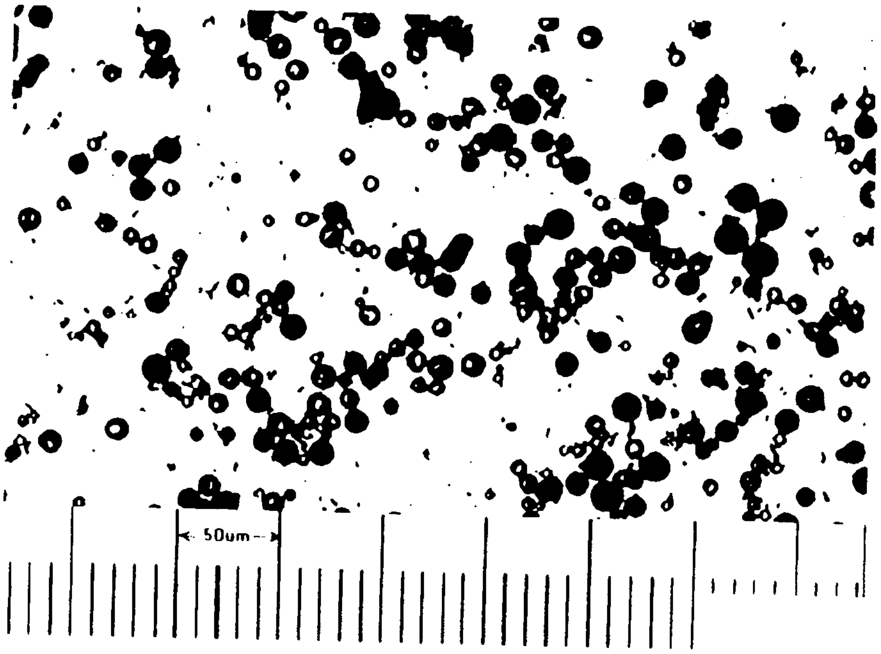

FIG. 2

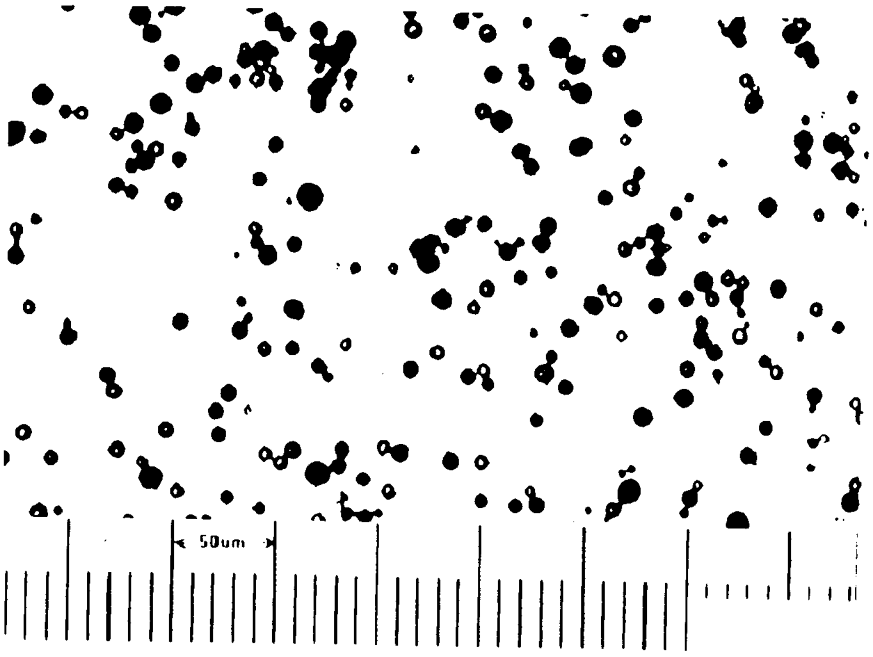

FIG. 3

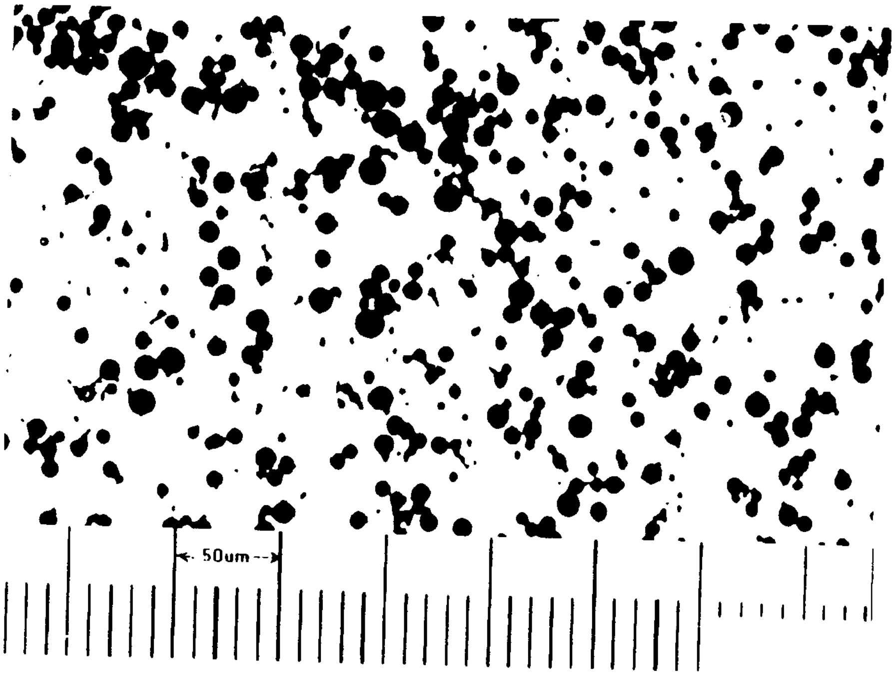

FIG. 4

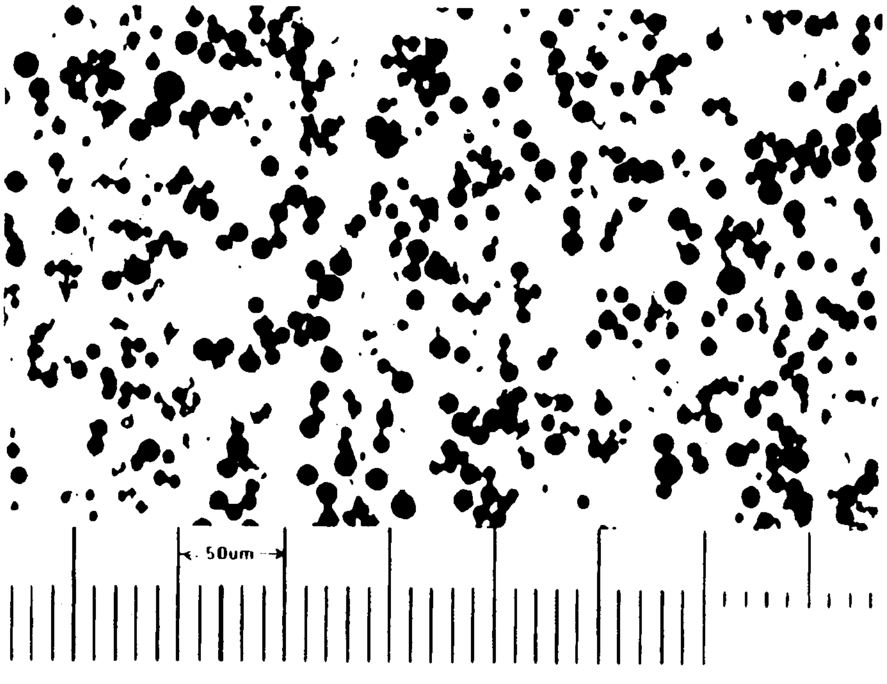

FIG. 5

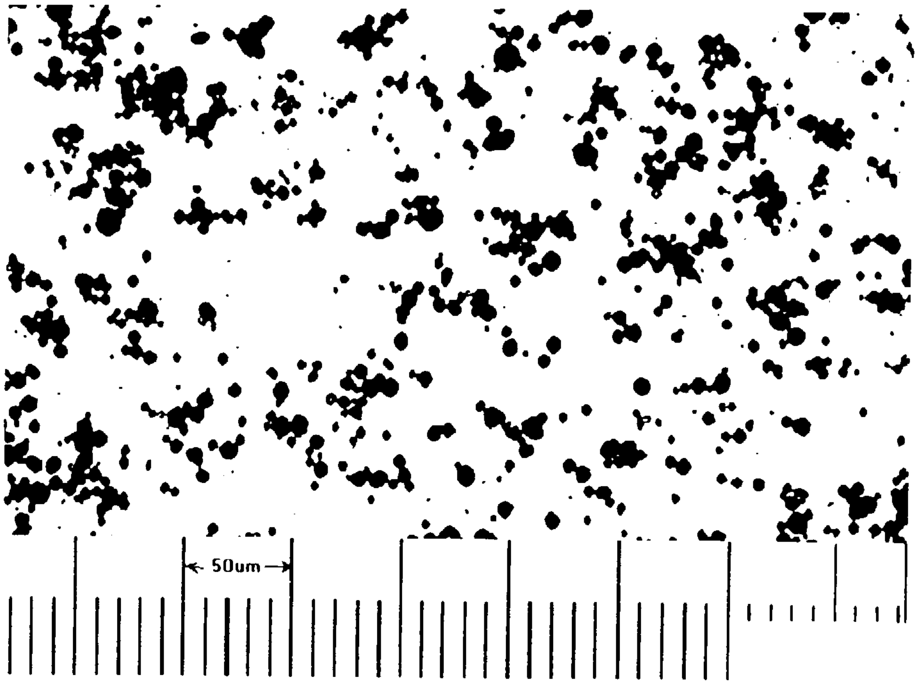

FIG. 6

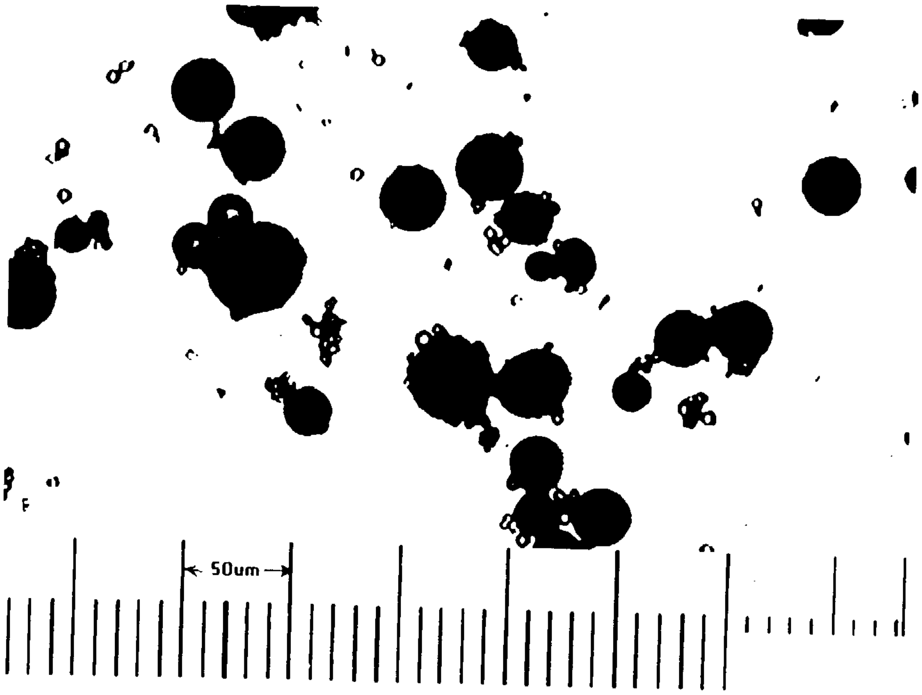

FIG. 7

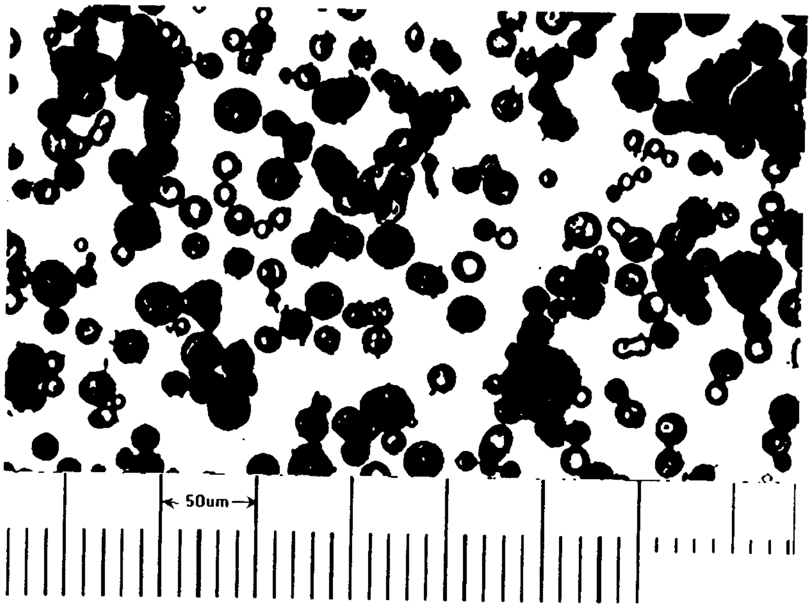
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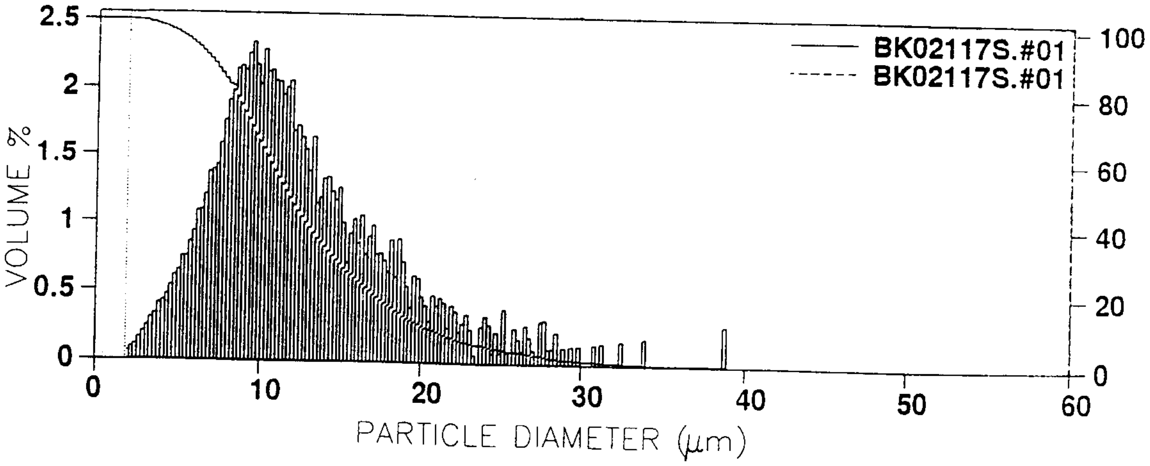
FIG. 8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1
0.5
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VOLUME %
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20
30
40
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FIG. 9

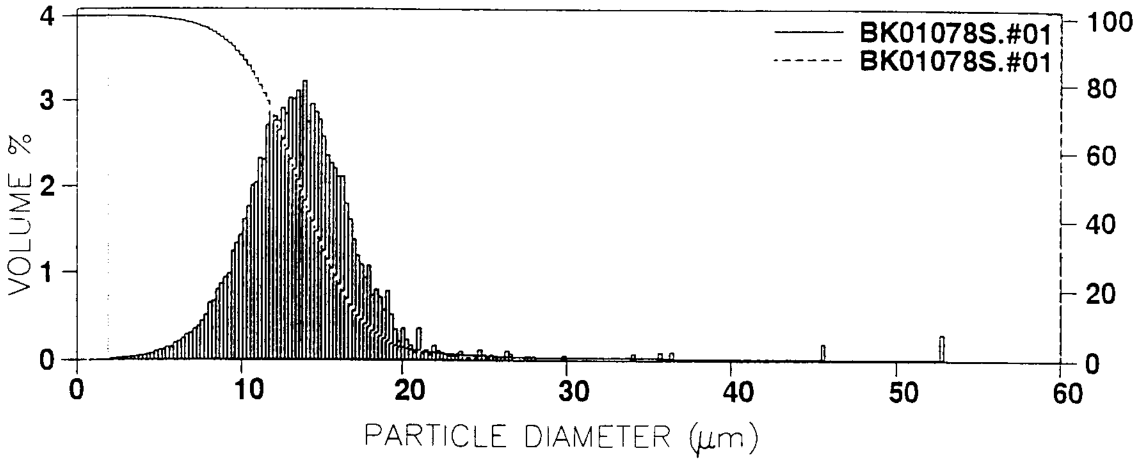
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FIG. 10

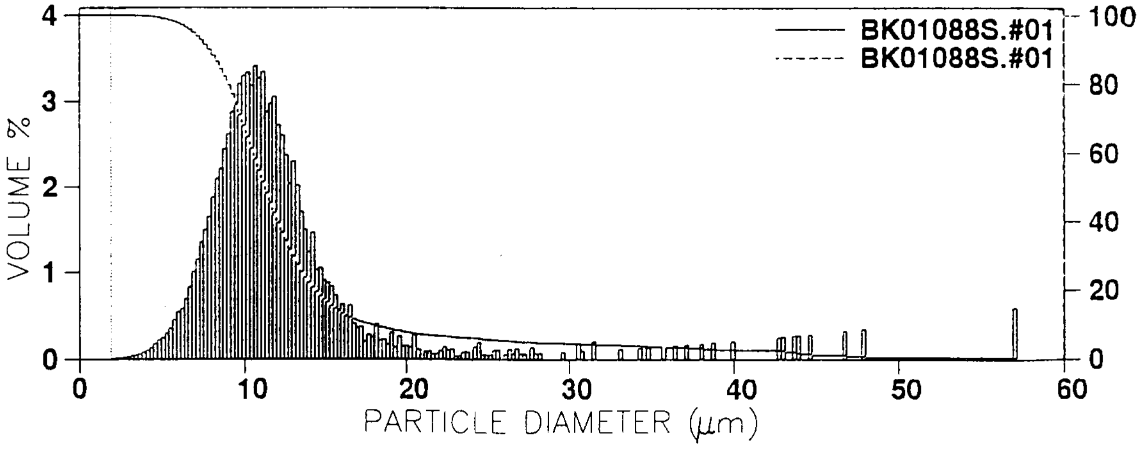
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FIG. 11

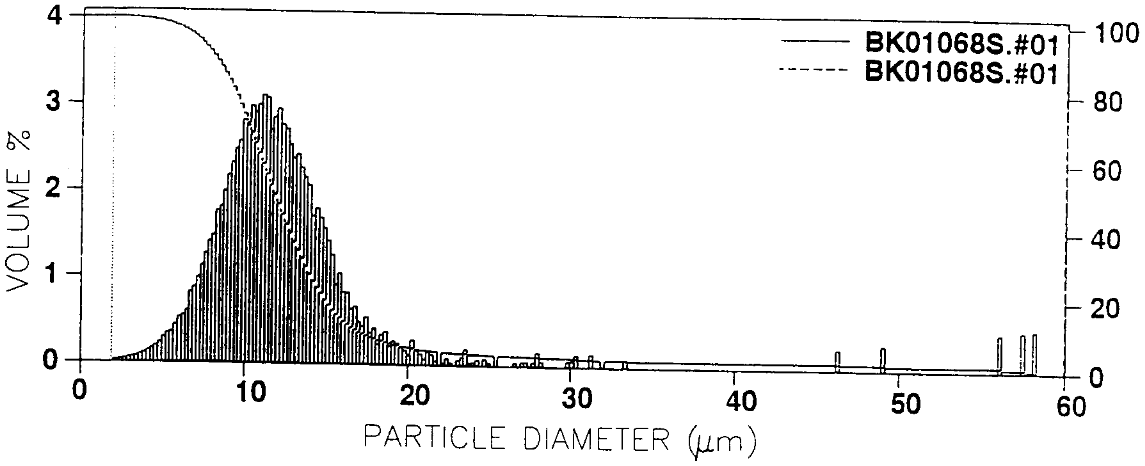
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FIG. 12

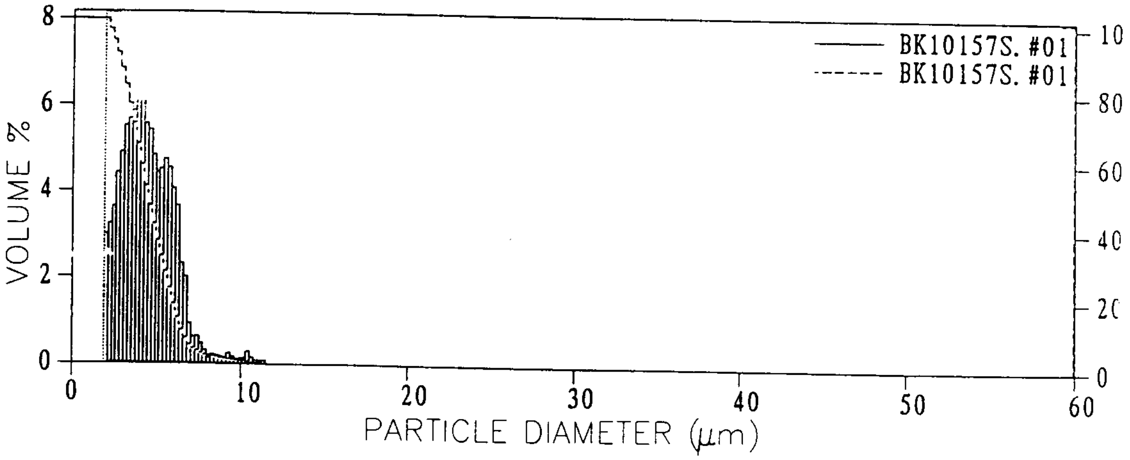
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FIG. 13

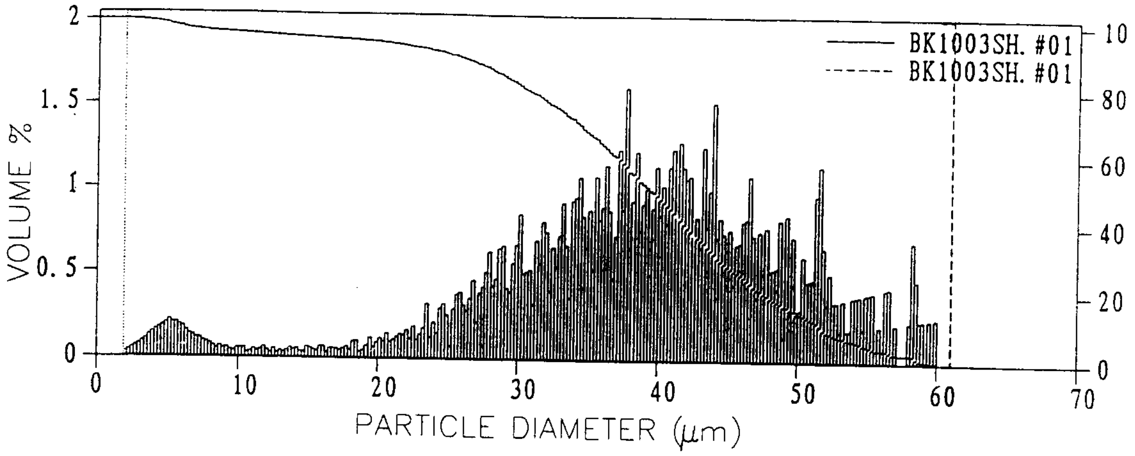
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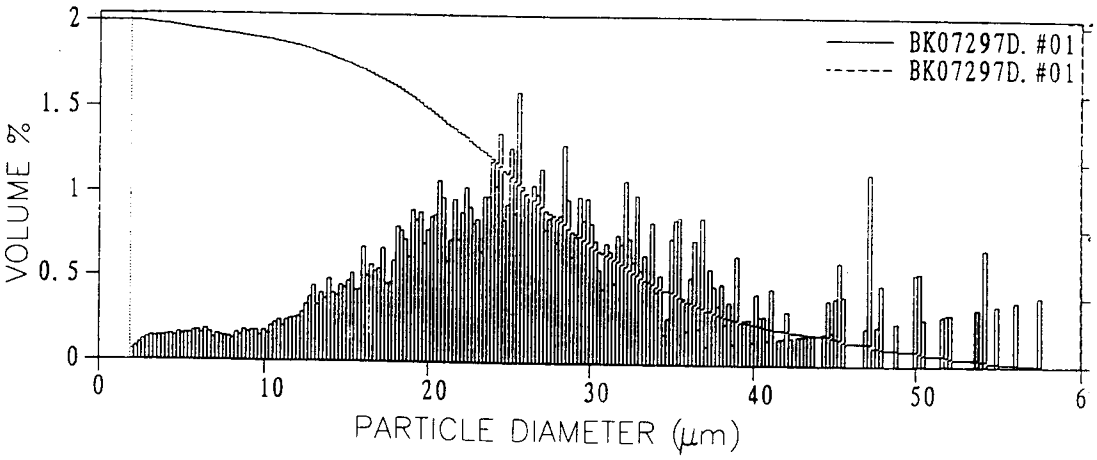
FIG. 14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50
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PARTICLE DIAMETER (μm)
BK07297D. #01
BK07297D. #01

European Patent Office

EUROPEAN SEARCH REPORT

Application Number
EP 99 30 1453

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
Y	DE 42 02 462 A (M.HUBER) 5 August 1993 * claim 1; examples 1-4 * ---	1-11	G03G9/08 G03G9/097
Y	EP 0 230 041 A (CANON) 29 July 1987 * page 5, line 26 - line 39; claims 1,8-11; examples 1,2 * ---	1-11	
Y	EP 0 376 343 A (CANON) 4 July 1990 * example 1 * ---	1-11	
A	EP 0 371 811 A (MITA) 6 June 1990 * claim 1 * ---	1-11	
Y	PATENT ABSTRACTS OF JAPAN vol. 13, no. 57 (P-825), 9 February 1989 & JP 63 247760 A (CANON), 14 October 1988 * abstract * -----	1-11	
			TECHNICAL FIELDS SEARCHED (Int.Cl.6)
			G03G

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	4 June 1999	Vanhecke, H

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04-06-1999

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
DE 4202462 A	05-08-1993	NONE	
EP 230041 A	29-07-1987	JP 1711489 C	11-11-1992
		JP 3076749 B	06-12-1991
		JP 62151862 A	06-07-1987
		DE 3688061 A	22-04-1993
		US 4845007 A	04-07-1989
EP 376343 A	04-07-1990	DE 68926611 D	11-07-1996
		DE 68926611 T	31-10-1996
		JP 2275964 A	09-11-1990
		JP 2749922 B	13-05-1998
		US 5130220 A	14-07-1992
EP 371811 A	06-06-1990	JP 1973293 C	27-09-1995
		JP 2147602 A	06-06-1990
		JP 6099491 B	07-12-1994
		JP 2047326 C	25-04-1996
		JP 2148046 A	06-06-1990
		JP 7069635 B	31-07-1995
		DE 68924579 D	23-11-1995
		DE 68924579 T	28-03-1996
		DE 68928351 D	30-10-1997
		DE 68928351 T	09-04-1998
		EP 0606930 A	20-07-1994
		JP 3220203 A	27-09-1991
		US 5104764 A	14-04-1992

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