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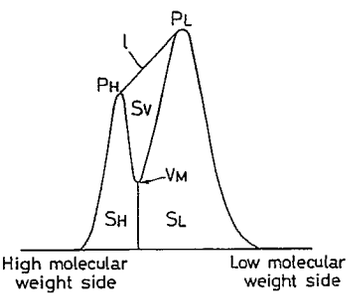
(54) Electrophotographic toner.

(57) The present invention provides an electrophotographic toner containing, as a fixing resin, a styrene-acrylic copolymer having a specific molecular-weight distribution and, as a coloring agent, carbon black having dibutyl phthalate oil absorption of not less than 80ml/100g, the toner presenting relaxation time of 10 to 50 ms at frequency of 100 kHz. The electrophotographic toner restrains the occurrence of defective fixing and off-set, and may be properly applied to a high-speed copying apparatus and a copying apparatus having a fixing unit so adapted as to consume less electric power.

Fig. 1



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BACKGROUND OF THE INVENTION

The present invention relates to an electrophotographic toner and more particularly to an electrophotographic toner to be used for image forming with the use of an electrostatic copying apparatus, a laser beam printer or the like.

In conventional image forming, a developer containing an electrophotographic toner is first held on the outer peripheral surface of a developing sleeve incorporating magnetic polarities, thereby to form a so-called magnetic brush. Then, the magnetic brush is brought in contact with a photoreceptor on the surface of which an electrostatic latent image is being formed, so that the electrophotographic toner in the developer electrostatically adheres to the electrostatic latent image. This causes the electrostatic latent image to be turned into a toner image. Then, the toner image is transferred to paper from the surface of the photoreceptor and fixed on the paper by fixing rollers. Thus, image forming is completed.

As the electrophotographic toner used for the image forming above-mentioned, there may be used an electrophotographic toner as obtained by blending a fixing resin with a coloring agent such as carbon black, a charge controlling agent and the like and by pulverizing the blended body into particles having sizes in a predetermined range.

The electrophotographic toner above-mentioned may present the problem of so-called off-set such as contamination of paper at the reverse side thereof due to adhesion of toner or contamination of the fixing rollers caused by separation of the toner from paper. In particular, when the fixing temperature is low, the toner image might not be satisfactorily fixed onto the paper (deterioration of fixing properties at a low temperature).

Of the problems above-mentioned, the deterioration of fixing properties at a low temperature occurs mainly when the molecular weight of the fixing resin contained in the electrophotographic toner is high. On the other hand, the off-set occurs mainly when the molecular weight of the fixing resin is low.

To overcome the problems above-mentioned, there have been proposed various examples of an electrophotographic toner jointly containing resin having low molecular weight and resin having high molecular weight (See, for example, Japanese Patent Unexamined Publications No. 16144/1981 and No. 3644/1985).

The electrophotographic toner set forth in the Publication No. 16144/1981 above-mentioned contains, as a fixing resin, a polymer obtainable by synthesizing a vinyl-type monomer, or a mixture of the polymer above-mentioned, which presents a chromatogram as obtained by a gel permeation chromatography in which at least one maximum value appears in both molecular-weight ranges from 10^3 to 8×10^4 and from 10^5 to 2×10^4.

The electrophotographic toner set forth in the Publication No. 3644/1985 above-mentioned mainly contains a fixing resin having the following three components:

A) Component of which weight-average molecular weight is not less than 500 000,

B) Component of which weight-average molecular weight is in a range from 20 000 to 200 000, and

C) Component of which weight-average molecular weight is in a range from 1 000 to 20 000.

The high molecular-weight component is excellent in resistance to off-set, but apt to decrease the fixing properties of the electrophotographic toner. The low molecular-weight component is excellent in fixing properties at a low temperature, but apt to decrease the resistance to off-set. It is therefore almost impossible to compatibly satisfy both fixing properties at a low temperature and resistance to off-set merely by jointly using both components. Further, in a resin containing both high and low molecular-weight components, the resin composition may be uneven or the resin cohesive force may be low. This involves the likelihood that the durability of the electrophotographic toner is lowered, causing the toner to be crushed during developing process. Further, toner which does not contribute to image forming (spent toner), may be increased in amount, thus disadvantageously accelerating the deterioration of the developer.

With the recent demand for a copying apparatus to be operated at a higher speed and with less power consumption, there is observed the tendency that the fixing time is shortened and the fixing temperature is lowered. Accordingly, a conventional electrophotographic toner presents the problems of defective fixing, increase in off-set phenomenon and shorter life-time of toner. Any effective countermeasures against such problems have not been found so far.

The inventors of the present invention have made a collective study on the molecular-weight distribution of a fixing resin and toner characteristics, and then found the following fact. That is, a styrene-acryl copolymer may be advantageously used as the fixing resin and, when high and low molecular-weight components are jointly used as the styrene-acryl copolymer, there may be advantageously used a great amount of a component common in both high and low molecular weight components, i.e., a component having an intermediate molecular weight. In this case, the resulting toner is improved in uniformity and

durability with defective fixing and off-set restrained.

However, it has also been found impossible to obtain, merely by selecting the type of fixing resin and setting the molecular-weight distribution thereof, an electrophotographic toner which can satisfactorily respond to the demands for higher-speed fixing and lower fixing-temperature with the recent advance of technology.

With the electrophotographic toner above-mentioned, there is a possibility of the fixed image being coarse and presenting apparent fog. The apparent fog refers to fog which is visually observed, even though the fog density is low when the formed image is optically measured with the use of an image analyzer or the like. Further, a toner image which is coarse or presents apparent fog above-mentioned, is low in surface smoothness. Accordingly, such a toner image may not be satisfactorily fixed and readily separated from the paper due to friction.

Repeated image forming with the electrophotographic toner above-mentioned presents the problems of defective image quality, decrease in image density and increase in the amount of toner which does not contribute to image forming (spent toner).

When image forming is repeated, the agitation of the developing device causes toner particles to receive a mechanical pressure, an impact force, frictional heat and the like, so that a toner aggregate is grown, causing the image to be grained. Further, the toner cannot be uniformly molten to lower the uniformity of the image quality. Further, the growth of toner aggregate presents the problem of a so-called blanking phenomenon. The blanking refers to the phenomenon that the toner aggregate grown with repeated image forming is caught between the paper and the surface of the photoreceptor to form gaps at the time when the tomer image is transferred to the paper, so that toner particles around the toner aggregate are not transferred to the paper, thus leaving a white image. **SUMMARY OF THE INVENTION**

To overcome the defects above-mentioned in the conventional electrophotographic toner, the present invention is proposed with the object of providing an electrophotographic toner to be properly used in a high-speed copying apparatus or a copying apparatus provided with a fixing unit so designed as to consume less electric power.

To solve the object above-mentioned, the inventors of the present invention have studied other factors than the fixing resin, and found that the dispersibility of carbon black as a coloring agent with respect to the fixing resin and the relaxation time of electrophotographic toner are important factors for restraining the defective fixing or off-set above-mentioned. Based on this finding, the inventors have completed the present invention.

According to a first embodiment of the present invention, there is provided an electrophotographic toner which contains, as a fixing resin, a styrene-acrylic copolymer presenting a gel permeation chromatogram of molecular-weight distribution in which the maximum value is located in each of the ranges of not less than 1×10^5 and from 500 to 2×10^4, and which also contains, as a coloring agent, carbon black of which dibutyl phthalate oil absorption is not less than 80ml/100g, the toner presenting relaxation time of 10 to 50 ms at a frequency of 100 kHz.

It is another object of the present invention to provide an electrophotographic toner with which an image as fixed is not coarse and does not present apparent fog.

To solve the object above-mentioned, the inventors of the present invention have studied the causes of coarse image and apaprent fog, and found that the coarse image is apt to be formed more often as the number of large-diameter coarse particles is increased and that the apparent fog is produced when such large toner particles as to be visually seen stick to the white parts of an image. The inventors have further studied the particle-size distribution of the electrophotographic toner. Based on this study, the present invention was accomplished.

According to a second embodiment of the present invention, there is provided an electrophotographic toner which contains, as a fixing resin, a styrene-acrylic copolymer having the molecular-weight distribution above-mentioned, and which presents a particle-size distribution in which a volumetric median diameter D_{50} as measured with a coulter counter is in a range from 7 to 13 μm and in which the ratio of particles having a particle size of not less than 16μm is not greater than 0,90% in terms of the number of particles.

It is a further object of the present invention to provide an electrophotographic toner which presents no problems of defective image quality, decrease in image density and increase in the amount of spent toner when development is repeated.

To solve the object above-mentioned, the inventors of the present invention have studied the causes of defective image quality, decrease in image density and increase in the amount of spent toner, and found that such problems are caused by improper particle-size distribution of the electrophotographic toner.

More specifically, when image forming is repeated with an electrophotographic toner containing a great amount of large-size particles, small-size toner particles apt to be readily electrostatically charged, are first

consumed, so that the ratio of large-size toner particles in the particle-size distribution is increased with passing time. Large-size toner particles provoke a decreasein resolution or a coarse image. Further, large-size toner particles are less electrostatically charged. This decreases the charge amount of the developer in its entirety, causing the toner to be scattered. This may provoke fog. The toner is apt to be more readily scattered under a high-temperature and high-humidity atmosphere where the toner charge amount is lowered.

On the other hand, when image forming is repeated with an electrophotographic toner containing a great amount of small-size particles, the small-size particles cause the developer to be lowered in flowability and are meltingly bonded to one another to increase the amount of the spent toner. Further, since the small-size particles present small adhering areas at the time of image fixing. This decreases the image density. Further, the small-size particles themselves are light-weight and readily scattered. Accordingly, when the charge amount undergoes a change with the increase in the amount of spent toner, there is a possibility of the small-size particles being scattered, thereby producing fog.

The electrophotographic toner has been further studied on the particle-size distribution thereof in other viewpoint than that in the second embodiment. Based on this study, the present invention was accomplished.

According to a third embodiment of the present invention, there is provided an electrophotographic toner which contains, as a fixing resin, a styrene-acrylic copolymer having the molecular-weight distribution above-mentioned, and which presents a particle-size distribution in which a volumetric median diameter D_{50} as measured with a coulter counter is in a range from 7 to 13 μm and in which the ratio of a 75% residual particle size D_{75} to a 25% residual particle size D_{25} (D_{25}/D_{75}) is in a range from 1,3 to 1,7.

The inventors of the present invention have found that the toner aggregate provoking blanking is caused by the presence of those high and low molecular-weight components contained in the styrene-acrylic copolymer of which molecular weights are respectively over and below certain levels.

More specifically, a polymer component of which molecular weight exceeds a certain level, is poor in elasticity, causing the component to be readily pulverized. On the other hand, a polymer component of which molecular weight is below a certain level, is high in stickness. This causes the toner particles to be bonded to one another, or causes pulverized micro-fine particles to be bonded to the toner particles. Accordingly, when image forming is repeated, the pulverization and bonding above-mentioned proceed, so that a toner aggregate is grown. In this connection, the upper and lower limits in the molecular-weight distribution of the fixing resin have been further studied, and based on this study, the present invention was accomplished.

According to a fourth embodiment of the present invention, there is provided an electrophotographic toner which contains, as a fixing resin, a styrene-acrylic copolymer presenting a gel permeation chromatogram of molecular-weight distribution in which the maximum value appears in each of the ranges of not less than 1×10^5 and from 500 to 2×10^4, and in which a detection starting molecular weight corresponding to the upper limit of the molecular weight is not greater than 2×10^8 and a detection ending molecular weight corresponding to the lower limit of the molecular weight is not less than 300.

In the electrophotographic toner of each of the first to fourth embodiments above-mentioned, there is preferably used, as the fixing resin, a styrene-acrylic copolymer having a molecular-weight distribution in which the minimum value is located between the two maximum values and in which the ratio of the total sum of the two peak areas respectively containing the two maximum values to the area of the valley part containing the minimum value and located below a common tangential line which connects the two peaks to each other, is not greater than 0,30.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 is a gel permeation chromatogram showing the molecular-weight distribution of a styrene-acrylic copolymer;

Figure 2 is a gel permeation chromatogram showing an example of a method of obtaining a styrene-acrylic copolymer presenting the molecular-weight distribution shown in Figure 1;

Figure 3 is a gel permeation chromatogram showing the molecular-weight distribution of a styrene-acrylic copolymer used in Example 16 and Comparative Example 24; and

Figure 4 is a gel permeation chromatogram showing the molecular-weight distribution of a styrene-acrylic copolymer used in Example 17 and Comparative Example 25.

Detailed Description of the Invention

There is used, as a fixing resin, a styrene-acrylic copolymer presenting a gel permeation chromatogram of molecular-weight distribution in which maximum values P_H and P_L are respectively located in the high molecular-weight side and the low molecular-weight side, as shown in Fig. 1.

The maximum value P_H at the high molecular-weight side should be not less than 1×10^5. If the molecular weight of the maximum value P_H is less than 1×10^5, the high molecular-weight component in the styrene-acrylic copolymer is insufficient in amount, thus failing to produce an electrophotographic toner excellent in resistance to off-set.

The molecular weight of the maximum value P_L at the low molecular-weight side should be in a range from 500 to 2×10^4. If the molecular weight of the maximum value P_L exceeds 2×10^4, the low molecular-weight component in the styrene-acrylic copolymer is insufficient in amount, thus failing to produce an electrophotographic toner excellent in fixing properties at a low temperature. On the other hand, if the molecular weight of the maximum value P_L is less than 500, the styrene-acrylic copolymer is insufficient in retention, thus failing to produce an electrophotographic toner excellent in durability.

Preferably used is a styrene-acrylic copolymer having a molecular-weight distribution in which the minimum value V_M is located between the maximum values P_H and P_L, as shown in Fig. 1.

The molecular weight of the minimum value V_M is not particularly limited to a certain value, as far as it is located between the molecular weights of both maximum values P_H and P_L.

A ratio (V/P) is introduced from the following equation:

$$V/P = \frac{S_V}{S_H + S_L}$$

where

S_H : Area of the peak part containing the maximum value P_H,

S_L : Area of the peak part containing the maximum value P_L, and

S_V : Area of the valley part containing the minimum value V_M and located below a common tangential line ℓ which connects both peaks.

The ratio (V/P) represents how the curve of molecular-weight distribution of the styrene-acrylic copolymer is approximated to a quadrilateral formed by connecting both maximum values with the common tangential line ℓ. As the ratio (V/P) is smaller, the curve is more approximated to a quadrilateral. This serves as an index which shows the amount of the intermediate molecular-weight component which lies between high and low molecular-weight components. More specifically, as the ratio (V/P) is smaller, the amount of the intermediate molecular-weight component is greater. This makes it possible to produce an electrophotographic toner having the optimum combination of fixing properties, resistance to off-set and durability.

According to the present invention, the ratio (V/P) is preferably not greater than 0,30, and more preferably not greater than 0,20. When the (V/P) exceeds 0,30, the amount of the intermediate molecular-weight component contained in the styrene-acrylic copolymer is insufficient. This deteriorates the uniformity and durability of the electrophotographic toner, and cannot restrain defective fixing and offset.

No particular restrictions are imposed on the ratio of the area S_H of the peak part containing the maximum value P_H at the high molecular-weight component side to the area S_L of the peak part containing the maximum value P_L at the low molecular-weight component side. However, such a ratio (S_H:S_L) is preferably in a range from 15:85 to 50:50, and more preferably from 20:80 to 45:55.

To produce the styrene-acrylic copolymer having the molecular-weight distribution above-mentioned, there are available three methods, i.e., a method of increasing the variance of the low molecular-weight component (molecular-weight distribution of M_W/M_N), a method of increasing the variance of the high molecular-weight component (M_W/M_N), and a method of increasing the variance of the high and low molecular-weight components (M_W/M_N). Generally, it is preferable to increase the variance of the high molecular-weight component (M_W/M_N) in view of various characteristics of electrophotographic toner. The variance of the high molecular-weight component (M_W/M_N) is preferably in a range from 2,7 to 3,7, and more preferably from 3,0 to 3,4. The variance of the low molecular-weight component (M_W/M_N) is preferably in a range from 1,5 to 2,5 and more preferably from 1,8 to 2,2.

The styrene-acrylic copolymer to be used in the present invention may be produced either by tightly

Note: M_W = weight average molecular weight M_N = number average molecular weight

melting and blending a plurality of types of styrene-acrylic copolymers having different molecular-weight distributions, or by using a two-stage polymerization.

For example, as shown in Fig. 2, when there are molten and blended, in the same amount, a styrene-acrylic copolymer (low molecular-weight component) having a molecular-weight distribution shown by a curve A and a styrene-acrylic copolymer (high molecular-weight component) having a molecular-weight distribution shown by a curve B, there is obtained a styrene-acrylic copolymer having a molecular-weight distribution, as shown by a curve C, which is located in the range determined in the present invention.

According to a suspension polymerization or an emulsion polymerization, a copolymer having a high molecular weight may generally be more easily produced as compared with a solution polymerization. Accordingly, the styrene-acrylic copolymer having the molecular-weight distribution above-mentioned may be produced by a multi-stage polymerization in which the suspension polymerization or the emulsion polymerization and the solution polymerization are combined in this order or in the reverse order with the molecular weight adjusted at each stage. The molecular weight or molecular-weight distribution may be adjusted by suitably selecting the type or amount of an initiator, the type of a solvent, a dispersing agent or an emulsifying agent relating to chain transfer, and the like.

As a styrene monomer, there may be used vinyl-toluene, α-methylstyrene or the like, besides styrene. As an acrylic monomer, there may be used a monomer represented by the following general formula (I):

$$CH_2 = \underset{\displaystyle R^1}{\overset{\displaystyle |}{C}} - CO - O - R^2 \qquad \cdots(I)\ ,$$

[R^1 is a hydrogen atom or a lower alkyl group, R^2 is a hydrogen atom, a hydrocarbon group having 1 to 12 carbon atoms, a hydroxyalkyl group, a vinylester group or an aminoalkyl group].

Examples of the acrylic monomer represented by the general formula (I), include acrylic acid, methacrylic acid, methyl acrylate, ethyl acrylate, butyl acrylate, 2-ethylhexyl acrylate, cyclohexyl acrylate, phenyl acrylate, methyl methacrylate, hexyl methacrylate, 2-ethylhexyl methacrylate, ethyl β-hydroxyacrylate, propyl γ-hydroxyacrylate, butyl δ-hydroxyacrylate, ethyl β-hydroxymethacrylate, propyl γ-aminoacrylate, propyl γ-N,N-diethylaminoacrylate, ethylene glycol dimethacrylate, tetraethylene glycol dimethacrylate and the like.

A styrene/methyl methacrylate/butyl acrylate copolymer may be used as the styrene-acrylic copolymer suitably used for the present invention. There may be preferably used a styrene/methyl methacrylate/butyl acrylate copolymer containing 75 to 85 % by weight of styrene, 0,5 to 5 % by weight of methyl methacrylate and 10 to 20 % by weight of butyl acrylate.

The electrophotographic toner in accordance with the first embodiment of the present invention may be produced by blending the styrene-acrylic copolymer above-mentioned with carbon black as a coloring agent and conventional additives such as a charge controlling agent and the like. In the toner, the relaxation time at frequency of 100 kHz which represents the charge characteristics of the toner, is limited to a range of 10 to 50 ms . If the relaxation time is shorter than 10 ms , the electric charge of the toner sticked to the photoreceptor disappears in a short period of time. This deteriorates the transferring ability, causing the resulting image to be defective in quality. An electrophotographic toner having bad charge characteristics is apt to be readily scattered in the developing unit or the like of an image forming apparatus. This may provoke contamination of paper, a blot on a formed image or the like. If the relaxation time exceeds 50 ms , the electric charge hardly gets away. This deteriorates a so-called cleaning ability, i.e., the removal of toner from the surface of the photoreceptor. The electrophotographic toner of which relaxation time exceeds 50 ms , is apt to readily stick to the fixing rollers and the like when the toner rubs against the fixing rollers and the like. This may provoke a defective image or contamination inside of the image forming apparatus.

As will be discussed later, the relaxation time may be adjusted to the range above-mentioned by suitably selecting the type and particle size of carbon black, the blending ratio and the like.

As to the carbon black, its dibutyl phthalate oil absorption (as measured by the method A stipulated in JIS K 6221-1982 "Testing Methods of Carbon Black for Rubber Industry") which serves as a factor of determining the dispersibility to the fixing resin, should be not less than 80 ml/100 g, and is preferably in a range from 90 to 120 ml/100 g. If the dibutyl phthalate oil absorption of carbon black is smaller than 80 ml/100 g, the dispersibility to the styrene-acrylic copolymer is insufficient. This deteriorates the uniformity and durability of the electrophotographic toner, and involves the likelihood that carbon black separated from broken resin contaminates the carrier which forms a developer together with the electrophotographic toner.

This accelerates the deterioration of the developer. On the other hand, if the dibutyl phthalate oil absorption of carbon black is smaller than 80 ml/100 g, the electric charge readily gets away to the outside through carbon black which is not being sufficiently dispersed in the styrene-acrylic copolymer. This causes the relaxation time to be shorter than the period of time of 10 ms above-mentioned. Accordingly, the electrophotographic toner is hardly charged. Further, carbon black which is not sufficiently dispersed and exposed from the surfaces of toner particles, may readily induce toner agglomeration or roller contamination at the fixing step.

The particle size of carbon black is not limited to a specific value, but is preferably in a range from 10 to 50 nm. If the particle size exceeds 50 nm, there is a possibility of the carbon black preventing the pulverization of electrophotographic toner. If the particle size of carbon black is smaller than 10 nm, the dispersibility of carbon black with respect to the styrene-acrylic copolymer is lowered. This may induce poor durability and carrier contamination, or may present a variety of problems resulting from poor charge characteristics.

The blending ratio of the carbon black in the electrophotographic toner is not limited to a specific value, but is preferably in a range from 3 to 20 % by weight. If the blending ratio of carbon black is less than 3 % by weight, the relaxation time of the electrophotographic toner might exceed 50 ms dependent on the particle size and dibutyl phthalate oil absorption of the carbon black. On the other hand, if the carbon black blending ratio exceeds 20 % by weight, the relaxation time might be less than 10 ms .

As the carbon black above-mentioned, there may be used any of various conventional carbon blacks such as furnace black, channel black, thermal, gas black, oil black, acetylene black and the like.

The particle size of the electrophotographic toner in accordance with the first embodiment is generally in a range from 5 to 20 μm, and preferably from 7 to 13 μm. The toner in such a range may be obtained by grinding, classification, suspension polymerization or the like.

The electrophotographic toner in accordance with the second embodiment of the present invention contains, as the fixing resin, a styrene-acrylic copolymer having the molecular-weight distribution mentioned earlier, and presents a toner particle-size distribution in which a volumetric median diameter D_{50} as measured with a coulter counter is in a range from 7 to 13 μm and in which the ratio of particles with a particle size of not less than 16μm being not greater tnan 0,90% in terms of the number of particles.

The following will discuss the reason why the toner particle-size distribution is limited to the range above-mentioned.

With an image analyzing apparatus, there was obtained a histogram of particle-size distribution of sticked toner particles on the white parts of a formed image before the image is fixed. The histogram was checked to obtain the relationship between the particle size and the coarseness or apparent fog of the image. Then, it was found that the image was coarse and presented apparent fog when the volumetric median diameter D_{50} as measured with a coulter counter exceeded 13 μm or when the ratio of the toner particles having particle size of not less than 16 μm in the electrophotographic toner exceeded 0,90% in terms of the number of particles even though the volumetric median diameter D_{50} was not greater than 13 μm. On the other hand, it was found that if the volumetric median diameter D_{50} was smaller than 7μm, the image was not coarse and presented no apparent fog but the image density was disadvantageously lowered. Thus, according to the present invention, the volumetric median diameter D_{50} is limited to the range from 7 to 13 μm and the ratio of the particles having a particle size of not less than 16 μm is limited to not greater than 0,90% in terms of the number of particles.

To adjust the particle-size distribution of the electrophotographic toner to the range above-mentioned, there may be suitably carried out grinding, classification, suspension polymerization and the like.

The electrophotographic toner in accordance with the second embodiment above-mentioned may be produced by blending the styrene-acrylic copolymer having the molecular-weight distribution above-mentioned with a coloring agent and conventional additives such as a charge controlling agent and the like.

The electrophotographic toner in accordance with the third embodiment of the present invention contains, as a fixing resin, a styrene-acrylic copolymer having the molecular-weight distribution above-mentioned, and presents a toner particle-size distribution in which a volumetric median diameter D_{50} as measured with a coulter counter is in a range from 7 to 13 μm and in which the ratio of a 75% residual particle size D_{75} to a 25% residual particle size D_{25} (D_{25}/D_{75}) is in a range from 1,3 to 1,7.

The following will discuss the reason why the toner particle-size distribution is limited to the range above-mentioned.

If the volumetric median diameter D_{50} as measured with a coulter counter is smaller than 7 μm or the ratio of a 75% residual particle size D_{75} to a 25% residual particle size D_{25} (D_{25}/D_{75}) is smaller than 1,3, the ratio of small particles in the electrophotographic toner is increased. This provokes a decrease in image density, an increase in the amount of spent toner, fog and the like. On the other hand, if the volumetric

median diameter D_{50} exceeds 13 μm, the ratio of large particles in the electrophotographic toner is increased, causing the image quality to be defective. If the ratio D_{25}/D_{75} exceeds 1,7, the ratio of large particles in the electrophotographic toner is increased, causing the image quality to be defective. Further, if the ratio D_{25}/D_{75} exceeds 1,7, the width of the molecular-weight distribution is broadened. This causes both ratios of large and small particles to be increased, thus provoking a decrease in image density, an increase in the amount of spent toner and defective image quality. Thus, according to the present invention, the volumetric median diameter D_{50} is limited to the range of 7 to 13 μm and the ratio of the 75% residual particle size D_{75} to the 25% residual particle size D_{25} (D_{25}/D_{75}) is limited to the range from 1,3 to 1,7.

The upper limit of the 25% residual particle size D_{25} is preferably in a range from 11,5 to 14,0 μm dependent on the value of the median diameter D_{50} or the 75% residual particle size D_{75}. The lower limit of the 75% residual particle size D_{75} is preferably in a range from 6,0 to 10 μm dependent on the value of the median diameter D_{50} or the 25% residual particle size D_{25}.

To adjust the particle-size distribution of the electrophotographic toner to the range above-mentioned, there may be suitably carried out grinding, classification, suspension polymerization and the like as done in the second embodiment.

The electrophotographic toner in accordance with the third embodiment above-mentioned may be produced by blending the styrene-acrylic copolymer having the molecular-weight distribution above-mentioned with a coloring agent and conventional additives such as a charge controlling agent and the like.

In the electrophotographic toner in accordance with the fourth embodiment of the present invention, the styrene-acrylic copolymer presents a molecular-weight distribution in which a detection starting molecular weight corresponding to the upper limit of the molecular-weight distribution is limited to not greater than 2×10^8 and a detection ending molecular weight corresponding to the lower limit of the molecular-weight distribution is limited to not less than 300.

If the detection starting molecular weight exceeds 2×10^8, the toner particles are apt to be readily pulverized. This does not only provoke a blanking phenomenon due to the growth of a toner aggregate, but also produces fog, variations of image quality and the like due to scattering of pulverized fine particles. If the detection ending molecular weight is smaller than 300, the toner particles are increased in adhesion. This does not only provoke a blanking phenomenon due to the growth of a toner aggregate, but also produces a granularly image. Further, the particles cannot be uniformly molten lowering the uniformity of image quality. Thus, according to the present invention, the detection starting molecular weight corresponding to the upper limit of the molecular-weight distribution is limited to not greater than 2×10^8 and the detection ending molecular weight corresponding to the lower limit of the molecular-weight distribution is limited to not less than 300.

When producing the styrene-acrylic copolymer having the molecular-weight distribution above-mentioned by the two-stage polymerization above-mentioned, it is preferable to polymerize the low molecular-weight component under relatively slow polymerization conditions and to polymerize the high molecular-weight component under relatively fast polymerization conditions.

When the low molecular-weight component is polymerized under the relatively slow polymerization conditions, the polymerization reaction sufficiently proceeds to prevent the formation of an extremely low molecular-weight component of which molecular weight is lower than 300. When the high molecular-weight component is polymerized under the relatively fast polymerization conditions, the polymerization reaction does not sufficiently proceed to prevent the formation of an extremely high molecular-weight component of which molecular weight exceeds 2×10^8. To adjust the polymerization conditions as above-mentioned, there may be suitably selected the types and blending amounts of the polymerization initiator and polymeric monomers, the polymerization temperature, the timing at which the materials are added to the polymeric system, and the like.

To produce, by the melting and blending method above-mentioned, the styrene-acrylic copolymer having the molecular-weight distribution above-mentioned, there may be used a low molecular-weight component polymerized under relatively slow polymerization conditions and a high molecular-weight component polymerized under relatively fast polymerization conditions.

The electrophotographic toner in accordance with the fourth embodiment of the present invention has the average particle size in a range from 5 to 20 μm and preferably from 7 to 13 μm. Toner having the particle size in the range above-mentioned may be obtained by grinding, classification, suspension polymerization or the like.

The electrophotographic toner in accordance with the fourth embodiment of the present invention may be produced by blending the styrene-acrylic copolymer having the molecular-weight distribution above-mentioned with a coloring agent and conventional additives such as a charge controlling agent and the like.

As the coloring agent to be used for producing the electrophotographic toner of each of the second to

fourth embodiments of the present invention, there may be used any of various conventional pigments and dyes to be used for coloring the toner.

The following will set forth suitable examples of the coloring agent.

Black

Carbon black such as furnace black, channel black, thermal, gas black, oil black, acetylene black and the like, Lamp black, Aniline black.

White

Zinc white, Titanium oxide, Antimony white, Zinc sulfide.

Red

Red iron oxide, Cadmium red, Red lead, Mercury cadmium sulfide, Permanent red 4R, Lithol red, Pyrazolone red, Watching red calcium salt, Lake red D, Brilliant carmine 6B, Eosine lake, Rhodamine lake B, Alizarine lake, Brilliant carmine 3B,

Orange

Chrome orange, Molybdenum orange, Permanent orange GTR, Pyrazolone orange, Vulcan orange, Indanthrene brilliant orange RK, Benzidine orange G, Indanthrene brilliant orange GK.

Yellow

Chrome yellow, Zinc yellow, Cadmium yellow, Yellow iron oxide, Mineral fast yellow, Nickel titanium yellow, Naples yellow, Naphthol yellow S, Hansa yellow G, Hansa yellow 10G, Benzidine yellow G, Benzidine yellow GR, Quinoline yellow lake, Permanent yellow NCG, Tartrazine lake.

Green

Chrome green, Chromium oxide, Pigment green B, Malachite green lake, Fanal yellow green G.

Violet

Manganese violet, Fast violet B, Methyl violet lake.

Blue

Prussian blue, Cobalt blue, Alkali blue lake, Victoria blue lake, Partially chlorinated phthalocyanine blue, Fast sky blue, Indanthrene blue BC.

As the coloring agent above-mentioned, there may also be used an extender pigment or a pigment made of a magnetic material. Examples of the extender pigment include Baryte powder, barium carbonate, clay, silica, white carbon, talc, alumina white. Examples of the pigment made of a magnetic material include: triiron tetroxide (Fe_3O_4), iron sesquioxide (γ-Fe_2O_3), zinc iron oxide ($ZnFe_2O_4$), yttrium iron oxide ($Y_3Fe_5O_{12}$), cadmium iron oxide ($CdFe_2O_4$), gadolinium iron oxide ($Gd_3Fe_5O_4$), copper iron oxide ($CuFe_2O_4$), lead iron oxide ($PbFe_{12}O_{19}$), neodymium iron oxide ($NdFeO_3$), barium iron oxide ($BaFe_{12}O_{19}$), magnesium iron oxide ($MgFe_2O_4$), manganese iron oxide ($MnFe_2O_4$), lanthanum iron oxide ($LaFeO_3$), iron powder, cobalt powder, nickel powder and the like. According to the present invention, any fine powder of these known magnetic materials may be used.

The electrophotographic toner may contain such a coloring agent in a ratio from 1 to 80 % by weight and preferably from 5 to 60 % by weight.

Examples of the charge controlling agent to be used for the electrophotographic toner in accordance with the present invention include: an oil-soluble dye such as nigrosine dye, oil black, spiron black and the like; metallic soap such as metallic naphthenate, metallic salicylate, metallic complex salicylate, metallic octylate, metallic fatty acid, metallic resinate and the like; a metal-containing monoazo dye; a pyrimidine compound; alkyl salicylic acid metal chelate and the like.

The electrophotographic toner may contain the charge controlling agent in a range from 0,1 to 5 % by weight.

As other additives than the charge controlling agent above-mentioned, there may be used an off-set preventing agent such as waxes including paraffin wax, polypropylene having a low molecular weight, polyethylene having a low molecular weight, fatty acid amide, silicone oil or the like, preferably in a ratio of 0,5 to 10 % by weight.

To improve the flowability, the toner particles may be coated at the surfaces thereof with a conventional surface treating agent which includes inorganic fine particles such as hydrophobic silica fine particles, carbon black or the like, resinous fine particles such as fluoroplastics particles, or the like.

The toner of the present invention may be mixed with a magnetic carrier such as ferrite, iron powder or the like to form a two-component developer adapted to be used for image forming by developing, transferring and fixing an electrostatic latent image.

Examples

The following description will discuss the present invention with reference to Examples and Comparative Examples.

Example 1

There were mixed (i) 100 parts by weight of a styrene (St)/methyl methacrylate (MMA)/butyl acrylate (BA) copolymer [St:MMA:BA = 80:5:15 (ratio by weight)] having the following molecular-weight distribution, (ii) 8 parts by weight of carbon black of which dibutyl phthalate oil absorption was 100ml/100g and of which average particle size was 22 μm, (iii) 1 part by weight of a negative-polarity dye as the charge controlling agent, and (iv) 1 part by weight of low molecular-weight polypropylene as an off-set preventing agent. When molten and kneaded with the use of a heating roll mill, the resulting mixture was cooled, ground and classified to produce an electrophotographic toner having a volumetric median diameter of 12 μm. In the toner thus produced, the relaxation time at frequency of 100 kHz was 30 ms

Molecular-Weight Distribution:

1) Molecular weight of the maximum value P_H: 597000
2) Variance of the peak containing the maximum value P_H (M_W/M_N): 3,1
3) Area of the peak containing the maximum value P_H (S_H): 25
4) Molecular weight of the maximum value P_L: 12200
5) Variance of the peak containing the maximum value P_L (M_W/M_N):1,95
6) Area of the peak containing the maximum value P_L (S_L): 75
7) Molecular weight of the minimum value V_M: 130000
8) Area of the valley containing the minimum value V_M (S_V): 14
9) Ratio (V/P): 0,140.

The dibutyl phthalate oil absorption of the carbon black was measured according to the method A stipulated in JIS K 6221-1982 "Testing Methods of Carbon Black for Rubber Industry") as set below.

First, 20,00 g of a sample dried at 105+/-2°C for one hour was put in a mixing chamber of an Absortmeter (manufactured by Brabender Company and having a spring tension of 2,68kg/cm^3). The limit switch for measuring the torque of sample-agitating rotary blades installed in the mixing chamber of the Absortmeter was set to the position corresponding to 70% of the maximum torque. With the limit switch thus set, the rotary blades were rotated at a speed of 125 r.p.m. At the same time, dibutyl phthalate (specific gravity of 1,045 to 1,050) was dropped into the mixing chamber at a speed of 4 ml/minute from an automatic burette, causing the sample to absorb the dibutyl phthalate. When oil absorption almost came to an end, the torque of the rotary blades was suddenly increased to turn OFF the limit switch. According to the following equation, the dibutyl phthalate oil absorption (ml/100g) was calculated with the use of the amount of dibutyl phthalate consumed between the time when the dropping started and the time when the limit switch was turned OFF (Bml), and the weight of the sample in a dry state (A=20,00 ml):

$$\text{Dibutyl phthalate oil absorption} = \frac{\text{Bml}}{\text{Ag}} \times 100$$

Example 2

There was produced an electrophotographic toner having a volumetric median diameter of 12 μm in the same manner as in Example 1 except for the use of 100 parts by weight of a styrene (St)/methyl methacrylate (MMA)/butyl acrylate (BA) copolymer [St:MMA:BA = 75:5:20 (ratio by weight)] having the following molecular-weight distribution, instead of 100 parts by weight of the copolymer used in Example 1. In the electrophotographic toner thus produced, the relaxation time at frequency of 100 kHz was 26 ms .

Molecular-Weight Distribution:

1) Molecular weight of the maximum value P_H: 240000
2) Variance of the peak containing the maximum value P_H (M_W/M_N): 3,0
3) Area of the peak containing the maximum value P_H (S_H): 32
4) Molecular weight of the maximum value P_L: 11000
5) Variance of the peak containing the maximum value P_L (M_W/M_N): 2,2
6) Area of the peak containing the maximum value P_L (S_L): 68
7) Molecular weight of the minimum value V_M: 35000
8) Area of the valley containing the minimum value V_M (S_V): 4,8
9) Ratio (V/P): 0,048 .

Example 3

There was produced an electrophotographic toner having a volumetric median diameter of 12 μm in the same manner as in Example 1 except for the use of 100 parts by weight of a styrene (St)/methyl methacrylate (MMA)/butyl acrylate (BA) copolymer [St:MMA:BA = 80:10:10 (ratio by weight)] having the following molecular-weight distribution, instead of 100 parts by weight of the copolymer used in Example 1, and the use of 7 parts by weight of carbon black of which dibutyl phthalate oil absorption was 80ml/100g and of which average particle size was 20 μm, instead of 8 parts by weight of carbon black used in Example 1. In the electrophotographic toner thus produced, the relaxation time at frequency of 100 kHz was 24 ms .

Molecular-Weight Distribution:

1) Molecular weight of the maximum value P_H: 105000
2) Variance of the peak containing the maximum value P_H (M_W/M_N): 3,1
3) Area of the peak containing the maximum value P_H (S_H): 28
4) Molecular weight of the maximum value P_L: 12500
5) Variance of the peak containing the maximum value P_L (M_W/M_N): 1,9
6) Area of the peak containing the maximum value P_L (S_L): 72
7) Molecular weight of the minimum value V_M: 45000
8) Area of the valley containing the minimum value V_M (S_V): 20,2
9) Ratio (V/P): 0,202 .

Example 4

There was produced an electrophotographic toner having a volumetric median diameter of 12 μm in the same manner as in Example 3 except for the use of 12 parts by weight of carbon black of which dibutyl phthalate oil absorption was 100ml/100g and of which average particle size was 25 μm, instead of 7 parts by weight of carbon black used in Example 3. In the electrophotographic toner thus produced, the relaxation time at frequency of 100 kHz was 12 ms .

Example 5

There was produced an electrophotographic toner having a volumetric median diameter of 12 μm in the same manner as in Example 1 except for the use of 100 parts by weight of a styrene (St)/methyl methacrylate (MMA)/butyl acrylate (BA) copolymer [St:MMA:BA = 85:5:10 (ratio by weight)] having the following molecular-weight distribution, instead of 100 parts by weight of the copolymer used in Example 1, and the use of 7 parts by weight of carbon black of which dibutyl phthalate oil absorption was 80ml/100g

and of which average particle size was 20 μm, instead of 8 parts by weight of carbon black used in Example 1. In the electrophotographic toner thus produced, the relaxation time at frequency of 100 kHz was 45 ms .

Molecular-Weight Distribution:

1) Molecular weight of the maximum value P_H: 350000
2) Variance of the peak containing the maximum value P_H (M_W/M_N): 2,9
3) Area of the peak containing the maximum value P_H (S_H): 21
4) Molecular weight of the maximum value P_L: 620
5) Variance of the peak containing the maximum value P_L (M_W/M_N): 3,1
6) Area of the peak containing the maximum value P_L (S_L): 79
7) Molecular weight of the minimum value V_M: 105000
8) Area of the valley containing the minimum value V_M (S_V): 22
9) Ratio (V/P): 0,22 .

Comparative Example 1

There was produced an electrophotographic toner having a volumetric median diameter of 12 μm in the same manner as in Example 1 except for the use of 100 parts by weight of a styrene (St)/methyl methacrylate (MMA)/butyl acrylate (BA) copolymer [St:MMA:BA = 80:5:15 (ratio by weight)] having the following molecular-weight distribution, instead of 100 parts by weight of the copolymer used in Example 1. In the electrophotographic toner thus produced, the relaxation time at frequency of 100 kHz was 29 ms .

Molecular-Weight Distribution:

1) Molecular weight of the maximum value P_H: 330000
2) Variance of the peak containing the maximum value P_H (M_W/M_N): 2,9
3) Area of the peak containing the maximum value P_H (S_H): 31
4) Molecular weight of the maximum value P_L: 16500
5) Variance of the peak containing the maximum value P_L (M_W/M_N): 2,2
6) Area of the peak containing the maximum value P_L (S_L): 69
7) Molecular weight of the minimum value V_M: 80000
8) Area of the valley containing the minimum value V_M (S_V): 52,1
9) Ratio (V/P): 0,521 .

Comparative Example 2

There was produced an electrophotographic toner having a volumetric median diameter of 12 μm in the same manner as in Example 1 except for the use of 100 parts by weight of a styrene (St)/methyl methacrylate (MMA)/butyl acrylate (BA) copolymer [St:MMA:BA = 82:4:14 (ratio by weight)] having the following molecular-weight distribution, instead of 100 parts by weight of the copolymer used in Example 1. In the electrophotographic toner thus produced, the relaxation time at frequency of 100 kHz was 20 ms .

Molecular-Weight Distribution:

1) Molecular weight of the maximum value P_H: 85000
2) Variance of the peak containing the maximum value P_H (M_W/M_N): 3,0
3) Area of the peak containing the maximum value P_H (S_H): 24
4) Molecular weight of the maximum value P_L: 5000
5) Variance of the peak containing the maximum value P_L (M_W/M_N): 2,3
6) Area of the peak containing the maximum value P_L (S_L): 76
7) Molecular weight of the minimum value V_M: 10800
8) Area of the valley containing the minimum value V_M (S_V) : 15,2
9) Ratio (V/P): 0,152 .

Comparative Example 3

There was produced an electrophotographic toner having a volumetric median diameter of 12 μm in the same manner as in Example 1 except for the use of 8 parts by weight of carbon black of which dibutyl phthalate oil absorption was 60ml/100g and of which average particle size was 24 μm, instead of 8 parts by weight of carbon black used in Example 1. In the electrophotographic toner thus produced, the relaxation time at frequency of 100 kHz was 22 ms .

Comparative Example 4

There was produced an electrophotographic toner having a volumetric median diameter of 12 μm in the same manner as in Example 1 except for the application of kneading conditions different from those in Example 1. In the electrophotographic toner thus produced, the relaxation time at frequency of 100 kHz was 60 ms .

Comparative Example 5

There was produced an electrophotographic toner having a volumetric median diameter of 12 μm in the same manner as in Comparative Example 3 except for the application of kneading conditions different from those in Comparative Example 3. In the electrophotographic toner thus produced, the relaxation time at frequency of 100 kHz was 8 ms .

Comparative Example 6

There was produced an electrophotographic toner having a volumetric median diameter of 12 μm in the same manner as in Example 3 except for the use of 20 parts by weight of carbon black of which dibutyl phthalate oil absorption was 100ml/100g and of which average particle size was 22 μm, instead of 7 parts by weight of carbon black used in Example 3. In the electrophotographic toner thus produced, the relaxation time at frequency of 100 kHz was 9 ms .

100 Parts by weight of the electrophotographic toner of each of Examples and Comparative Examples above-mentioned was mixed with 0,2 part by weight of hydrophobic silica to produce a mixture. Blended with the mixture was ferrite carrier having an average particle size of 80 μm. The resultant mixture was uniformly agitated and mixed to produce a two-component developer having a toner density of 4.0%. The following tests were conducted on each of the developers thus obtained.

Copying Ability Test

With the use of each of the developers above-mentioned, 20 000 copies were taken with an electrophotographic copying apparatus (DC-5585 manufactured by Mita Industrial Co., Ltd.), after which the fixing rollers were checked for contamination. The transfer efficiency for 20 000 copies was calculated according to the following equation:

Transfer Efficiency(%) = Amount of toner transferred to the paper/Amount of toner consumed for copying

Fixing Property Test I

While the temperature set to the heating rollers of an electrophotographic copying apparatus (Modified Type of DC-5585 manufactured by Mita Industrial Co., Ltd.) (of the heating pressure roller fixing type) was raised in steps of 2,5 °C from 140 °C, paper having thereon a toner image corresponding to a solid-black document was passed in the apparatus, causing the image to be fixed. An adhesive tape was pressingly contacted with each fixed image and then separated. The density data of each fixed image before and after separation were measured with a reflection densitometer (manufactured by Tokyo Densyoku Co., Ltd.). According to the following equation, there was obtained the lowest temperature at which the fixing ratio was increased and exceeded 90%. This temperature was referred to as the lowest fixing temperature (F_1).

Fixing ratio (%) = (Image density after separa tion/Image density before separation) x 100.

While the roller temperature was further raised, there was obtained the temperature at which off-set occurred. This temperature was referred to as the high-temperature off-set generating temperature (F_2).

There was calculated the difference (F_2 -F_1) between the lowest fixing temperature (F_1) and the high-temperature off-set generating temperature (F_2). This difference was referred to as a fixing temperature range (FΔ).

Test of Resistance to Blocking

First, 20 g of each toner was put in a glass cylinder having an inner diameter of 26,5 mm in an oven of 60 °C. A weight of 100 g was placed on the toner, which was then left for 30 minutes. The cylinder was pulled out and the toner state was observed. The toner which collapsed and was turned into the original particles, was judged as no blocking (O), while the toner presenting a lump even slightly was judged as blocking (X).

Test of Resistance to Shock

Each developer before used for copying was sufficiently mixed, after which the toner was removed from the developer. The amount of carbon remaining in the carrier (CI) was measured. Further, the toner was removed from each developer which had been used for 20 000-piece continuous copying. The amount of carbon remaining in the carrier (CE) was measured. The spent toner generation ratio (s-value %) was obtained according to the following equation:

$$\text{s-value (\%)} = \text{CE-CI}\ .$$

The results of all the tests above-mentioned are shown in Table 1.

Table 1 (1/2)

	Test of Copying Ability I		Test of Resistance to Blocking
	Roller Contamination	Transfer Efficiency (%)	
Example 1	Absent	86	O
Example 2	Absent	83	O
Example 3	Absent	85	O
Example 4	Absent	80	O
Example 5	Absent	88	O
Comparative Example 1	Absent	84	X
Comparative Example 2	Absent	81	X
Comparative Example 3	Present	80	X
Comparative Example 4	Present	85	O
Comparative Example 5	Present	68	X
Comparative Example 6	Present	70	X

Table 1 (2/2)

	Test of Fixing Properties F_1 (°C)	F_2 (°C)	FΔ (°C)	s-value (%)
Example 1	150	190	40	0,15
Example 2	145	185	40	0,13
Example 3	140	180	40	0,31
Example 4	145	185	40	0,29
Example 5	150	190	40	0,16
Comparative Example 1	165	180	15	1,05
Comparative Example 2	150	180	30	1,10
Comparative Example 3	150	175	25	1,18
Comparative Example 4	150	175	25	0,14
Comparative Example 5	145	165	20	1,14
Comparative Example 6	140	175	35	0,93

From the results in Table 1, it was found that the electrophotographic toner of each of Examples 1 to 5 was excellent in fixing properties at a low temperature because the lowest fixing temperature (F_1) was low, the transfer efficiency was high and the rollers were not contaminated. It was also found that the electrophotographic toner of each of Examples 1 to 5 was excellent in resistance to off-set because the high-temperature off-set generating temperature (F_2) was high and no blocking was taken place in the test of resistance to blocking. It was also found that the electrophotographic toner of each of Examples 1 to 5 was excellent in resistance to shock because the spent toner producing ratio (s-value) was low, the transfer efficiency was high and the rollers were not contaminated. Thus, it was found that the electrophotographic toner of each of the Examples 1 to 5 of which fixing temperature range (FΔ) was broad, was properly applied to a high-speed copying apparatus or a copying apparatus having a fixing unit so arranged as to consume less electric power.

On the other hand, the electrophotographic toners of Comparative Examples 1 to 6 deviated from the scope of the present invention in any of the molecular-weight distribution of the styrene/methyl methacrylate/butyl acrylate copolymer, the dibutyl phthalate oil absorption of carbon black and the relaxation time at frequency of 100 kHz. It was found that the toners of such Comparative Examples were disadvantageous in any of the fixing properties at a low temperature, resistance to blocking or resistance to shock.

Example 6

There were mixed (i) 100 parts by weight of a styrene (St)/methyl methacrylate (MMA)/butyl acrylate

(BA) copolymer [St:MMA:BA = 80:5:15 (ratio by weight)] having the following molecular-weight distribution, (ii) 7 parts by weight of carbon black as a coloring agent, (iii) 1 part by weight of a negative-polarity dye as the charge controlling agent, and (iv) 1 part by weight of low molecular-weight polypropylene as an off-set preventing agent. When molten and kneaded, the resulting mixture was cooled, ground and classified to produce an electrophotographic toner which presented a volumetric median diameter D_{50} of 10,0 μm and in which the ratio of particles having a particle size of not less than 16 μm was 0,40% in terms of the number of particles.

Molecular-Weight Distribution:

1) Molecular weight of the maximum value P_H: 597000
2) Variance of the peak containing the maximum value P_H (M_W/M_N): 3,1
3) Area of the peak containing the maximum value P_H (S_H): 25
4) Molecular weight of the maximum value P_L: 12200
5) Variance of the peak containing the maximum value P_L (M_W/M_N): 1,95
6) Area of the peak containing the maximum value P_L (S_L): 75
7) Molecular weight of the minimum value V_M: 130000
8) Area of the valley containing the minimum value V_M (S_V): 14
9) Ratio (V/P): 0,140.

Example 7

There was produced an electrophotographic toner which presented a volumetric median diameter D_{50} of 11,2 μm and in which the ratio of particles having a particle size of not less than 16 μm was 0,55% in terms of the number of particles, in the same manner as in Example 6 except for the use of 100 parts by weight of a styrene (St)/methyl methacrylate (MMA)/butyl acrylate (BA) copolymer [St:MMA:BA = 75:5:20 (ratio by weight)] having the following molecular-weight distribution, instead of 100 parts by weight of the copolymer used in Example 6.

Molecular-Weight Distribution:

1) Molecular weight of the maximum value P_H: 240000
2) Variance of the peak containing the maximum value P_H (M_W/M_N): 3,0
3) Area of the peak containing the maximum value P_H (S_H): 32
4) Molecular weight of the maximum value P_L: 11000
5) Variance of the peak containing the maximum value P_L (M_W/M_N): 2,2
6) Area of the peak containing the maximum value P_L (S_L): 68
7) Molecular weight of the minimum value V_M: 35000
8) Area of the valley containing the minimum value V_M (S_V): 4,8
9) Ratio (V/P): 0,048 .

Example 8

There was produced an electrophotographic toner which presented a volumetric median diameter D_{50} of 7,8 μm and in which the ratio of particles having a particle size of not less than 16 μm was 0,35% in terms of the number of particles, in the same manner as in Example 6 except for the application of grinding and classifying conditions different from those in Example 6.

Example 9

There was produced an electrophotographic toner which presented a volumetric median diameter D_{50} of 7,8 μm and in which the ratio of particles having a particle size of not less than 16 μm was 0,83% in terms of the number of particles, in the same manner as in Example 6 except for the use of 100 parts by weight of a styrene (St)/methyl methacrylate (MMA)/butyl acrylate (BA) copolymer [St:MMA:BA = 80:10:10 (ratio by weight)] having the following molecular-weight distribution, instead of 100 parts by weight of the copolymer used in Example 6.

Molecular-Weight Distribution:

1) Molecular weight of the maximum value P_H: 105000
2) Variance of the peak containing the maximum value P_H (M_W/M_N): 3,1
3) Area of the peak containing the maximum value P_H (S_H): 28
4) Molecular weight of the maximum value P_L: 12500
5) Variance of the peak containing the maximum value P_L (M_W/M_N): 1,9
6) Area of the peak containing the maximum value P_L (S_L): 72
7) Molecular weight of the minimum value V_M: 45000
8) Area of the valley containing the minimum value V_M (S_V): 20,2
9) Ratio (V/P): 0,202.

Example 10

There was produced an electrophotographic toner which presented a volumetric median diameter D_{50} of 12,7 μm and in which the ratio of particles having a particle size of not less than 16 μm was 0,83% in terms of the number of particles, in the same manner as in Example 9 except for the application of grinding and classifying conditions different from those in Example 9.

Example 11

There was produced an electrophotographic toner which presented a volumetric median diameter D_{50} of 12,7 μm and in which the ratio of particles having a particle size of not less than 16 μm was 0,76% in terms of the number of particles, in the same manner as in Example 6 except for the use of 100 parts by weight of a styrene (St)/methyl methacrylate (MMA)/butyl acrylate (BA) copolymer [St:MMA:BA = 85:5:10 (ratio by weight)] having the following molecular-weight distribution, instead of 100 parts by weight of the copolymer used in Example 6.

Molecular-Weight Distribution:

1) Molecular weight of the maximum value P_H: 350000
2) Variance of the peak containing the maximum value P_H (M_W/M_N): 2,9
3) Area of the peak containing the maximum value P_H (S_H): 21
4) Molecular weight of the maximum value P_L: 620
5) Variance of the peak containing the maximum value P_L (M_W/M_N): 3,1
6) Area of the peak containing the maximum value P_L (S_L): 79
7) Molecular weight of the minimum value V_M: 105000
8) Area of the valley containing the minimum value V_M (S_V): 22
9) Ratio (V/P): 0,22 .

Comparative Example 7

There was produced an electrophotographic toner which presented a volumetric median diameter D_{50} of 10,5 μm and in which the ratio of particles having a particle size of not less than 16 μm was 0,55% in terms of the number of particles, in the same manner as in Example 6 except for the use of 100 parts by weight of a styrene (St)/methyl methacrylate (MMA)/butyl acrylate (BA) copolymer [St:MMA:BA = 83:5:12 (ratio by weight)] having the following molecular-weight distribution, instead of 100 parts by weight of the copolymer used in Example 6.

Molecular-Weight Distribution:

1) Molecular weight of the maximum value P_H: 600000
2) Variance of the peak containing the maximum value P_H (M_W/M_N): 3,0
3) Area of the peak containing the maximum value P_H (S_H): 70
4) Molecular weight of the maximum value P_L: 12000
5) Variance of the peak containing the maximum value P_L (M_W/M_N): 2,0
6) Area of the peak containing the maximum value P_L (S_L): 30
7) Molecular weight of the minimum value V_M: 70000
8) Area of the valley containing the minimum value V_M (S_V): 30,9
9) Ratio (V/P): 0,309.

Comparative Example 8

There was produced an electrophotographic toner which presented a volumetric median diameter D_{50} of 10,2 μm and in which the ratio of particles having a particle size of not less than 16 μm was 1,50% in terms of the number of particles, in the same manner as in Example 6 except for the application of grinding and classifying conditions different from those in Example 6.

Comparative Example 9

There was produced an electrophotographic toner which presented a volumetric median diameter D_{50} of 13,5 μm and in which the ratio of particles having a particle size of not less than 16 μm was 1,18% in terms of the number of particles, in the same manner as in Example 7 except for the application of grinding and classifying conditions different from those in Example 7.

Comparative Example 10

There was produced an electrophotographic toner which presented a volumetric median diameter D_{50} of 6,8 μm and in which the ratio of particles having a particle size of not less than 16 μm was 0,95% in terms of the number of particles, in the same manner as in Example 6 except for the application of grinding and classifying conditions different from those in Example 6.

Comparative Example 11

There was produced an electrophotographic toner which presented a volumetric median diameter D_{50} of 11,9 μm and in which the ratio of particles having a particle size of not less than 16 μm was 0,93% in terms of the number of particles, in the same manner as in Example 9 except for the application of grinding and classifying conditions different from those in Example 9.

Comparative Example 12

There was produced an electrophotographic toner which presented a volumetric median diameter D_{50} of 11,8 μm and in which the ratio of particles having a particle size of not less than 16 μm was 0,85% in terms of the number of particles, in the same manner as in Example 6 except for the use of 100 parts by weight of a styrene (St)/methyl methacrylate (MMA)/butyl acrylate (BA) copolymer [St:MMA:BA = 80:7:13 (ratio by weight)] having the following molecular-weight distribution, instead of 100 parts by weight of the copolymer used in Example 6.

Molecular-Weight Distribution:

1) Molecular weight of the maximum value P_H: 600000
2) Variance of the peak containing the maximum value P_H (M_W/M_N): 2,2
3) Area of the peak containing the maximum value P_H (S_H): 68
4) Molecular weight of the maximum value P_L: 22000
5) Variance of the peak containing the maximum value P_L (M_W/M_N): 2,8
6) Area of the peak containing the maximum value P_L (S_L): 32
7) Molecular weight of the minimum value V_M: 85000
8) Area of the valley containing the minimum value V_M (S_V): 28
9) Ratio (V/P): 0,28.

Comparative Example 13

There was produced an electrophotographic toner which presented a volumetric median diameter D_{50} of 13,3 μm and in which the ratio of particles having a particle size of not less than 16 μm was 0,87% in terms of the number of particles, in the same manner as in Example 11 except for the application of grinding and classifying conditions different from those in Example 11.

100 Parts by weight of the electrophotographic toner of each of Examples 6 to 11 and Comparative Examples 7 to 13 was mixed with 0,2 part by weight of hydrophobic silica to produce a mixture. Blended with the mixture was ferrite carrier having the average particle size of 80 μm. The resultant mixture was

uniformly agitated and mixed to produce a two-component developer having toner density of 4,0%. The following tests were conducted on each of the developers thus obtained.

Image-Quality Uniformity Test I

With an electrophotographic copying apparatus (DC-5585 manufactured by Mita Industrial Co., Ltd.) using each of the developers above-mentioned, a 20mm x 20mm solid-black document was copied. The image at the center portion of each reproduced image with the 2mm-wide peripheral edge thereof removed, was divided into 56 small sections. With a QTM display, there was measured the area ratio of the black (or white) portion of each small section. With the ratio value thus obtained, the average area ratio and the area ratio variation (standard deviation) were respectively calculated according to the following equations.

Average area ratio (%) = Total area ratio (%)/Number of small sections (=56).

$$\text{Area ratio standard deviation} = \sqrt{\frac{\Sigma(\text{Average area ratio} - \text{Individual small section area ratio})^2}{(\text{Number of small sections} - 1)(=55)}}$$

On comparison of the results of area ratio standard deviation with the results of organoleptic examination which was conducted by a plurality of persons, the coefficient of correlation r was 0,918. It therefore turned out that both results approximately agreed with each other. Thus, image-quality uniformity was evaluated based on the results of area ratio standard deviation. The image presenting an area ratio standard deviation of not greater than 3 was evaluated as excellent (O), the image presenting an area ratio standard deviation of not greater than 5 was evaluated as good (Δ), and the image presenting an area ratio standard deviation more than 5 was evaluated as bad (X).

Apparent Fog Test

A black-white document was copied with an electrophotographic copying apparatus (DC-5585 manufactured by Mita Industrial Co., Ltd.) using each of the developers above-mentioned. The white portion of each image before fixed was measured with an image analyzer (QUANTIMET 900 Image Analyzer manufactured by Cambridge Instruments Co., Ltd.), thereby to obtain a histogram of the particle-size distribution of sticked toner. From each histogram thus obtained, there was obtained the ratio of particles having particle size of not less than 16 μm to all the particles sticked to the white portion (% by the number of particles).

Fixing Property Test II

While the temperature set to the heating rollers of an electrophotographic copying apparatus (Modified Type of DC-5585 manufactured by Mita Industrial Co., Ltd.) (of the heating pressure roller fixing type) was raised in steps of 2,5°C from 140°C, paper having thereon a toner image corresponding to a solid-black document was passed in the apparatus, causing the image to be fixed, likewise in Fixing Property Test I. Placed on a rubber stand the transfer paper on which the toner image corresponding to the solid-black image had been fixed. A weight (20g/cm^2) made of cylindrical soft steel having a height of 26 mm and a diameter of 50 mm of which bottom surface was covered with a cotton cloth, was reciprocated on the transfer paper 5 times, causing the fixed image to be forcibly rubbed. According to the following equation, there was obtained the lowest temperature at which the fixing ratio was increased and exceeded 95%. This lowest temperature was referred to as a friction resistant temperature (F_3).

Fixing ratio (%) = (Image density after rub bing/Image density before rubbing) x 100.

Table 2 shows the results of the tests above-mentioned, together with the results of Fixing Property Test I, Test of Resistance to Blocking and Test of Resistance to Shock.

Table 2 (1/2)

	Image Characteristics		Test of Resistance to Blocking	s-value (%)
	Image Quality Uniformity	Apparent Fog (%)		
Example 6	O	2,0	O	0,13
Example 7	O	2,5	O	0,13
Example 8	O	1,8	O	0,14
Example 9	O	2,3	O	0,16
Example 10	O	2,9	O	0,15
Example 11	O	2,1	O	0,17
Comparative Example 7	Δ	2,7	X	0,87
Comparative Example 8	X	13,1	O	0,14
Comparative Example 9	X	11,2	O	0,15
Comparative Example 10	Δ	3,1	O	1,53
Comparative Example 11	Δ	3,5	O	0,18
Comparative Example 12	Δ	2,2	O	0,14
Comparative Example 13	Δ	2,1	X	0,16

Table 2 (2/2)

	Fixing Property Test			
	F_1 (°C)	F_2 (°C)	FΔ (°C)	F_3 (°C)
Example 6	140	195	55	145
Example 7	135	190	55	150
Example 8	145	190	45	140
Example 9	135	190	55	145
Example 10	140	190	50	145
Example 11	135	185	50	140
Comparative Example 7	160	180	20	165
Comparative Example 8	140	190	50	165
Comparative Example 9	135	190	55	165
Comparative Example 10	140	190	50	160
Comparative Example 11	140	190	50	155
Comparative Example 12	145	180	35	155
Comparative Example 13	140	190	50	145

From the results shown in Table 2, it was found that the electrophotographic toner of each of Examples 6 to 11 was excellent in fixing properties at a low temperature because the lowest fixing temperature (F_1) was low. It was also found that the electrophotographic toner of each of Examples 6 to 11 was excellent in resistance to off-set because the high-temperature off-set generating temperature (F_2) was high and no blocking was observed at Test of Resistance to Blocking. It was also found that the electrophotographic toner of each of Examples 6 to 11 was excellent in resistance to shock because the spent toner producing ratio (s-value) was low. From the fact of low friction resistant temperature (F_3) and from the test results of image-quality uniformity and apparent fog, it was found that, with the electrophotographic toner of each of Examples 6 to 11, the resultant fixed image was excellent in smoothness and free from coarseness and apparent fog.

On the other hand, the electrophotographic toners of Comparative Examples 7 to 13 deviated from the scope of the present invention in any of the molecular-weight distribution of the styrene/methyl methacrylate/butyl acrylate copolymer and the particle-size distribution. It was found that the toners of such Comparative Examples were disadvantageous in any of the characteristics above-mentioned.

Example 12

There were mixed (i) 100 parts by weight of a styrene (St)/methyl methacrylate (MMA)/butyl acrylate (BA) copolymer [St:MMA:BA = 80:5:15 (ratio by weight)] having the following molecular-weight distribution, (ii) 7 parts by weight of carbon black as a coloring agent, (iii) 1 part by weight of a negative-polarity dye as the charge controlling agent, and (iv) 1 part by weight of low molecular-weight polypropylene as an off-set preventing agent. When molten and kneaded, the resulting mixture was cooled, ground and classified to produce an electrophotographic toner presenting the following particle-size distribution.

Molecular-Weight Distribution:

1) Molecular weight of the maximum value P_H: 597000
2) Variance of the peak containing the maximum value P_H (M_W/M_N): 3,1
3) Area of the peak containing the maximum value P_H (S_H): 25
4) Molecular weight of the maximum value P_L: 12200
5) Variance of the peak containing the maximum value P_L (M_W/M_N): 1,95
6) Area of the peak containing the maximum value P_L (S_L): 75
7) Molecular weight of the minimum value V_M: 130000
8) Area of the valley containing the minimum value V_M (S_V): 14
9) Ratio (V/P): 0,140.

Particle-Size Distribution:

1) Median diameter D_{50}: 10,0
2) 25% residual particle size D_{25} : 12,5
3) 75% residual particle size D_{75} : 8,6
4) Ratio D_{25}/D_{75} : 1,46.

Example 13

There was produced an electrophotographic toner having the following particle-size distribution in the same manner as in Example 12 except for the use of 100 parts by weight of a styrene (St)/methyl methacrylate (MMA)/butyl acrylate (BA) copolymer [St:MMA:BA = 75:5:20 (ratio by weight)] having the following molecular-weight distribution, instead of 100 parts by weight of the copolymer used in Example 12.

Molecular-Weight Distribution:

1) Molecular weight of the maximum value P_H: 240000
2) Variance of the peak containing the maximum value P_H (M_W/M_N): 3,0
3) Area of the peak containing the maximum value P_H (S_H): 32
4) Molecular weight of the maximum value P_L: 11000
5) Variance of the peak containing the maximum value P_L (M_W/M_N): 2,2
6) Area of the peak containing the maximum value P_L (S_L): 68
7) Molecular weight of the minimum value V_M: 35000
8) Area of the valley containing the minimum value V_M (S_V): 4,8
9) Ratio (V/P): 0,048.

Particle-Size Distribution:

1) Median diameter D_{50}: 11,7
2) 25% residual particle size D_{25} : 13,2
3) 75% residual particle size D_{75} : 8,5
4) Ratio D_{25}/D_{75} : 1,55 .

Example 14

There was produced an electrophotographic toner having the following particle-size distribution in the same manner as in Example 12 except for the use of 100 parts by weight of a styrene (St)/methyl methacrylate (MMA)/butyl acrylate (BA) copolymer [St:MMA:BA = 75:5:20 (ratio by weight)] having the

following molecular-weight distribution, instead of 100 parts by weight of the copolymer used in Example 12.

Molecular-Weight Distribution:

1) Molecular weight of the maximum value P_H: 105000
2) Variance of the peak containing the maximum value P_H (M_W/M_N): 3,1
3) Area of the peak containing the maximum value P_H (S_H): 28
4) Molecular weight of the maximum value P_L: 12500
5) Variance of the peak containing the maximum value P_L (M_W/M_N): 1,9
6) Area of the peak containing the maximum value P_L (S_L): 72
7) Molecular weight of the minimum value V_M: 45000
8) Area of the valley containing the minimum value V_M (S_V): 20,2
9) Ratio (V/P): 0,202.

Particle-Size Distribution:

1) Median diameter D_{50}: 7,3
2) 25% residual particle size D_{25} : 10,5
3) 75% residual particle size D_{75} : 6,4
4) Ratio D_{25}/D_{75} : 1,63.

Example 15

There was produced an electrophotographic toner having the following particle-size distribution in the same manner as in Example 12 except for the use of 100 parts by weight of a styrene (St)/methyl methacrylate (MMA)/butyl acrylate (BA) copolymer [St:MMA:BA = 85:5:10 (ratio by weight)] having the following molecular-weight distribution, instead of 100 parts by weight of the copolymer used in Example 12.

Molecular-Weight Distribution:

1) Molecular weight of the maximum value P_H: 350000
2) Variance of the peak containing the maximum value P_H (M_W/M_N): 2,9
3) Area of the peak containing the maximum value P_H (S_H): 21
4) Molecular weight of the maximum value P_L: 620
5) Variance of the peak containing the maximum value P_L (M_W/M_N): 3,1
6) Area of the peak containing the maximum value P_L (S_L): 79
7) Molecular weight of the minimum value V_M: 105000
8) Area of the valley containing the minimum value V_M (S_V): 22
9) Ratio (V/P): 0,22.

Particle-Size Distribution:

1) Median diameter D_{50}: 12,8
2) 25% residual particle size D_{25} : 13,9
3) 75% residual particle size D_{75} : 8,97
4) Ratio D_{25}/D_{75} : 1,55 .

Comparative Example 14

There was produced an electrophotographic toner having the following particle-size distribution in the same manner as in Example 12 except for the application of grinding and classifying conditions different from those in Example 12.

Particle-Size Distribution:

1) Median diameter D_{50}: 10,2

2) 25% residual particle size D_{25} : 13,4
3) 75% residual particle size D_{75} : 7,3
4) Ratio D_{25}/D_{75} : 1,84.

Comparative Example 15

There was produced an electrophotographic toner having the following particle-size distribution in the same manner as in Example 13 except for the application of grinding and classifying conditions different from those in Example 13.

Particle-Size Distribution:

1) Median diameter D_{50}: 10,4
2) 25% residual particle size D_{25} : 11,0
3) 75% residual particle size D_{75} : 8,8
4) Ratio D_{25}/D_{75} : 1,25.

Comparative Example 16

There was produced an electrophotographic toner having the following particle-size distribution in the same manner as in Example 12 except for the application of grinding and classifying conditions different from those in Example 12.

Particle-Size Distribution:

1) Median diameter D_{50}: 12,9
2) 25% residual particle size D_{25} : 14,8
3) 75% residual particle size D_{75} : 8,5
4) Ratio D_{25}/D_{75} : 1,75.

Comparative Example 17

There was produced an electrophotographic toner having the following particle-size distribution in the same manner as in Example 13 except for the application of grinding and classifying conditions different from those in Example 13.

Particle-Size Distribution:

1) Median diameter D_{50}: 6,8
2) 25% residual particle size D_{25} : 7,9
3) 75% residual particle size D_{75} : 6,5
4) Ratio D_{25}/D_{75} : 1,20.

Comparative Example 18

There was produced an electrophotographic toner having the following particle-size distribution in the same manner as in Example 12 except for the use of 100 parts by weight of a styrene (St)/methyl methacrylate (MMA)/butyl acrylate (BA) copolymer [St:MMA:BA = 80:10:10 (ratio by weight)] having the following molecular-weight distribution, instead of 100 parts by weight of the copolymer used in Example 12.

Molecular-Weight Distribution:

1) Molecular weight of the maximum value P_H: 330000
2) Variance of the peak containing the maximum value P_H (M_W/M_N): 2,8
3) Area of the peak containing the maximum value P_H (S_H): 31
4) Molecular weight of the maximum value P_L: 16500
5) Variance of the peak containing the maximum value P_L (M_W/M_N): 2,3

6) Area of the peak containing the maximum value P_L (S_L): 69
7) Molecular weight of the minimum value V_M: 90000
8) Area of the valley containing the minimum value V_M (S_V): 30,9
9) Ratio (V/P): 0,309.

Particle-Size Distribution:

1) Median diameter D_{50}: 10,2
2) 25% residual particle size D_{25} : 12,5
3) 75% residual particle size D_{75} : 8,0
4) Ratio D_{25}/D_{75} : 1,56.

Comparative Example 19

There was produced an electrophotographic toner having the following particle-size distribution in the same manner as in Example 14 except for the application of grinding and classifying conditions different from those in Example 14.

Particle-Size Distribution:

1) Median diameter D_{50}: 10,2
2) 25% residual particle size D_{25} : 13,8
3) 75% residual particle size D_{75} : 7,9
4) Ratio D_{25}/D_{75} : 1,74.

Comparative Example 20

There was produced an electrophotographic toner having the following particle-size distribution in the same manner as in Example 14 except for the application of grinding and classifying conditions different from those in Example 14.

Particle-Size Distribution:

1) Median diameter D_{50}: 10,4
2) 25% residual particle size D_{25} : 11,0
3) 75% residual particle size D_{75} : 8,8
4) Ratio D_{25}/D_{75} : 1,25.

Comparative Example 21

There was produced an electrophotographic toner having the following particle-size distribution in the same manner as in Example 14 except for the application of grinding and classifying conditions different from those in Example 14.

Particle-Size Distribution:

1) Median diameter D_{50}: 14,3
2) 25% residual particle size D_{25} : 16,1
3) 75% residual particle size D_{75} : 10,5
4) Ratio D_{25}/D_{75} : 1,53.

Comparative Example 22

There was produced an electrophotographic toner having the following particle-size distribution in the same manner as in Example 14 except for the application of grinding and classifying conditions different from those in Example 14.

Particle-Size Distribution:

1) Median diameter D_{50}: 6,6
2) 25% residual particle size D_{25} : 8,1
3) 75% residual particle size D_{75} : 5,6
4) Ratio D_{25}/D_{75} : 1,44.

Comparative Example 23

There was produced an electrophotographic toner having the following particle-size distribution in the same manner as in Example 15 except for the application of grinding and classifying conditions different from those in Example 15.

Particle-Size Distribution:

1) Median diameter D_{50}: 12,6
2) 25% residual particle size D_{25} : 13,8
3) 75% residual particle size D_{75} : 10,7
4) Ratio D_{25}/D_{75} : 1,28.

100 Parts by weight of the electrophotographic toner of each of Examples 12 to 15 and Comparative Examples 14 to 23 was mixed with 0,2 part by weight of hydrophobic silica to produce a mixture. Blended with the mixture was ferrite carrier having the average particle size of 80 μm. The resultant mixture was uniformly agitated and mixed to produce a two-component developer having toner density of 4,0%. The following tests were conducted on each of the developers thus obtained.

Measurement of Initial Image Density

With an electrophotographic copying apparatus (DC-5585 manufactured by Mita Industrial Co., Ltd.) using each of the developers above-mentioned, a solid-black document was copied. The density of each copied image was measured with a reflection densitometer (TC-6D manufactured by Tokyo Densyoku Co., Ltd.).

Measurement of Initial Resolution

With an electrophotographic copying apparatus (DC-5585 manufactured by Mita Industrial Co., Ltd.) using each of the developers above-mentioned, a diagram sheet for measuring resolution in accordance with JIS B 7174-1962 was copied to obtain the resolution of each copied image (lines/mm).

Image Density Preservation Test I

With an electrophotographic copying apparatus (DC-5585 manufactured by Mita Industrial Co., Ltd.) using each of the developers above-mentioned, a solid-black document was copied for 20 000 pieces under high-temperature and high-humidity conditions (35 °C and relative humidity of 85%). By extracting every thousandth copied piece, total 21 copied pieces were extracted, as samples, from 20 000 copied pieces for each developer. With a reflection densitometer (TC-6D manufactured by Tokyo Denshoku Co., Ltd.), the density of the copied image of each sample was measured, and the number of samples of which image density was not less than 1,3, was obtained. The developer with which there were obtained 20 or more samples, out of the total 21 samples, presenting an image density not less than 1,3, was evaluated as excellent (O), the developer with which there were obtained 15 to 19 samples presenting an image density not less than 1,3, was evaluated as good (Δ), and the developer with which there were obtained 14 or less samples presenting an image density not less than 1,3, was evaluated as bad (X).

Resolution Preservation Test

With an electrophotographic copying apparatus (DC-5585 manufactured by Mita Industrial Co., Ltd.) using each of the developers above-mentioned, a diagram sheet for measuring resolution in accordance with JIS B 7174-1962 was copied for 20 000 pieces under high-temperature and high-humidity conditions (35 °C and relative humidity of 85%). By extracting every thousandth copied piece, total 21 copied pieces were extracted, as samples, from 20 000 copied pieces for each developer. The resolution (lines/mm) of the copied image of each sample was obtained, and there was also obtained the number of samples presenting

resolution of not less than 6,3 lines/mm. The developer with which there were obtained 10 or more samples, out of the total 21 samples, presenting resolution not less than 6,3 lines/mm, was evaluated as excellent (O), the developer with which there were obtained 4 to 9 samples presenting resolution not less than 6,3 lines/mm, was evaluated as good (Δ), and the developer with which there were obtained 3 or less samples presenting resolution not less than 6,3 lines/mm, was evaluated as bad (X).

Toner Scattering Test

For each developer, there were checked (i) the white portions of 21 samples as extracted from 20 000 copied pieces taken from the resolution measuring diagram sheet above-mentioned, and (ii) the inside of the copying apparatus after 20 000 copies had been taken. The developer with which no toner scattering was observed on the samples and the inside of the copying apparatus, was evaluated as excellent (O), the developer with which toner scattering was ovserved inside of the copying apparatus but the copied images presented no practical problems, was evaluated as good (Δ), and the developer with which a great amount of scattering toner was ovserved on the samples and inside of the copying apparatus, was evaluated as bad (X).

Together with the results of the Fixing Property Test I and Test of Resistance to Shock, the results above-mentioned are shown in Table 3.

Table 3 (1/2)

	Fixing Property Test			s-value	Toner Scattering
	F_1 (°C)	F_2 (°C)	FΔ (°C)	(%)	
Example 12	140	195	55	0,16	O
Example 13	135	190	55	0,15	O
Example 14	140	190	50	0,18	O
Example 15	140	195	55	0,19	O
Comparative Example 14	145	190	45	0,32	Δ
Comparative Example 15	140	190	50	1,05	X
Comparative Example 16	145	190	45	0,31	Δ
Comparative Example 17	140	190	50	1,45	X
Comparative Example 18	145	180	35	1,15	X
Comparative Example 19	140	190	50	0,25	X
Comparative Example 20	150	190	40	0,83	X
Comparative Example 21	150	185	35	0,29	Δ
Comparative Example 22	155	195	40	0,95	X
Comparative Example 23	145	185	40	0,19	Δ

Table 3 (2/2)

	Initial Image Density	Image Density Preservation	Initial Resolution (lines/mm)	Resolution Preservation
Example 12	1,36	O	5,6	O
Example 13	1,37	O	5,0	O
Example 14	1,33	O	5,6	O
Example 15	1,41	O	5,0	O
Comparative Example 14	1,40	O	4,5	Δ
Comparative Example 15	1,26	X	5,0	Δ
Comparative Example 16	1,35	O	3,6	X
Comparative Example 17	0,90	X	5,0	O
Comparative Example 18	1,31	Δ	4,5	X
Comparative Example 19	1,41	O	3,6	X
Comparative Example 20	1,28	X	5,0	Δ
Comparative Example 21	1,44	O	3,6	X
Comparative Example 22	1,05	X	5,0	Δ
Comparative Example 23	1,42	O	4,5	X

From the results shown in Table 3, it was found that the electrophotographic toner of each of Examples 12 to 15 was excellent in fixing properties at a low temperature because the lowest fixing temperature (F_1) was low. It was also found that the electrophotographic toner of each of Examples 12 to 15 was excellent in resistance to off-set because the high-temperature off-set generating temperature (F_2) was high. It was also found that the electrophotographic toner of each of Examples 12 to 15 was excellent in resistance to shock because the spent toner producing ratio (s-value) was low. It was also found that the electrophotographic toner of each of Examples 12 to 15 was excellent in initial image density and image density preservation to prevent the image density from being lowered, and also presented excellent initial resolution & resolution preservation and no toner scattering to prevent the image quality to be defective.

On the other hand, the electrophotographic toners of Comparative Examples 14 to 23 deviated from the scope of the present invention in any of the molecular-weight distribution of the styrene/methyl methacrylate/butyl acrylate copolymer and the particle-size distribution. It was found that the toners of such Comparative Examples were disadvantageous in any of the characteristics above-mentioned.

Example 16

There were mixed (i) 100 parts by weight of a styrene (St)/methyl methacrylate (MMA)/butyl acrylate (BA) copolymer [St:MMA:BA = 80:5:15 (ratio by weight)] having the following molecular-weight distribution and presenting a gel permeation chromatogram shown by a solid line in Fig. 3, (ii) 8 parts by weight of carbon black, (iii) 1 part by weight of a negative-polarity dye as the charge controlling agent, and (iv) 1 part by weight of low molecular-weight polypropylene as an off-set preventing agent. When molten and kneaded with the use of a heating roll mill, the resulting mixture was cooled, ground and classified to produce an electrophotographic toner having a volumetric median diameter of 11 μm. In Fig. 3, the axis of ordinate represens the ratio (in %) of the height of each peak with respect to the height of the top peak in a gel permeation chromatogram which is set to 100.

Molecular-Weight Distribution:

1) Detection starting molecular weight (M_{START}): $3,6 \times 10^6$
2) Detection ending molecular weight (M_{END}): 390
3) Molecular weight of the maximum value P_H: 335000
4) Variance of the peak containing the maximum value P_H (M_W/M_N): 1,53
5) Area of the peak containing the maximum value P_H (S_H): 22
6) Molecular weight of the maximum value P_L: 13900
7) Variance of the peak containing the maximum value P_L (M_W/M_N): 2,30
8) Area of the peak containing the maximum value P_L (S_L): 78
9) Molecular weight of the minimum value V_M: 76000
10) Area of the valley containing the minimum value V_M (S_V): 21
11) Ratio (V/P): 0,210.

Example 17

There was produced an electrophotographic toner having a volumetric median diameter of 11 μm in the same manner as in Example 16 except for the use of 100 parts by weight of a styrene (St)/methyl methacrylate (MMA)/butyl acrylate (BA) copolymer [St:MMA:BA = 85:5:10 (ratio by weight)] having the following molecular-weight distribution and presenting a gel permeation chromatogram shown by a solid line in Fig. 4, instead of 100 parts by weight of the copolymer used in Example 16. Likewise in Fig. 3, the axis of ordinate in Fig. 4 represents the ratio (in %) of the height of each peak with respect to the height of the top peak in a gel permeation chromatogram which is set to 100.

Molecular-Weight Distribution:

1) Detection starting molecular weight (M_{START}): $3,6 \times 10^7$
2) Detecton ending molecular weight (M_{END}): 521
3) Molecular weight of the maximum value P_H: 435000
4) Variance of the peak containing the maximum value P_H (M_W/M_N): 2,32
5) Area of the peak containing the maximum value P_H (S_H): 25
6) Molecular weight of the maximum value P_L: 13300
7) Variance of the peak containing the maximum value P_L (M_W/M_N): 2,11
8) Area of the peak containing the maximum value P_L (S_L): 75
9) Molecular weight of the minimum value V_M: 72000
10) Area of the valley containing the minimum value V_M (S_V): 18,8
11) Ratio (V/P): 0,188.

Example 18

There was produced an electrophotographic toner having a volumetric median diameter of 11 μm in the

same manner as in Example 16 except for the use of 100 parts by weight of a styrene (St)/methyl methacrylate (MMA)/butyl acrylate (BA) copolymer [St:MMA:BA = 80:5:15 (ratio by weight)] having the following molecular-weight distribution, instead of 100 parts by weight of the copolymer used in Example 16.

Molecular-Weight Distribution:

1) Detection starting molecular weight (M_{START}): $1,6 \times 10^6$
2) Detection ending molecular weight (M_{END}): 470
3) Molecular weight of the maximum value P_H: 105000
4) Variance of the peak containing the maximum value P_H (M_W/M_N): 3.1
5) Area of the peak containing the maximum value P_H (S_H): 28
6) Molecular weight of the maximum value P_L: 12500
7) Variance of the peak containing the maximum value P_L (M_W/M_N): 1,9
8) Area of the peak containing the maximum value P_L (S_L): 72
9) Molecular weight of the minimum value V_M: 45000
10) Area of the valley containing the minimum value V_M (S_V): 20,2
11) Ratio (V/P): 0,202.

Comparative Example 24

There was produced an electrophotographic toner having a volumetric median diameter of 11 μm in the same manner as in Example 16 except for the use of 100 parts by weight of a styrene (St)/methyl methacrylate (MMA)/butyl acrylate (BA) copolymer [St:MMA:BA = 80:5:15 (ratio by weight)] having the following molecular-weight distribution and presenting a gel permeation chromatogram shown by a broken line in Fig. 3, instead of 100 parts by weight of the copolymer used in Example 16.

Molecular-Weight Distribution:

1) Detection starting molecular weight (M_{START}): $3,2 \times 10^8$
2) Detecton ending molecular weight (M_{END}): 382
3) Molecular weight of the maximum value P_H: 290100
4) Variance of the peak containing the maximum value P_H (M_W/M_N): 1,83
5) Area of the peak containing the maximum value P_H (S_H): 23
6) Molecular weight of the maximum value P_L: 13100
7) Variance of the peak containing the maximum value P_L (M_W/M_N): 2,04
8) Area of the peak containing the maximum value P_L (S_L): 77
9) Molecular weight of the minimum value V_M: 69000
10) Area of the valley containing the minimum value V_M (S_V): 20,6
11) Ratio (V/P): 0,206 .

Comparative Example 25

There was produced an electrophotographic toner having a volumetric median diameter of 11 μm in the same manner as in Example 16 except for the use of 100 parts by weight of a styrene (St)/methyl methacrylate (MMA)/butyl acrylate (BA) copolymer [St:MMA:BA = 83:5:12 (ratio by weight)] having the following molecular-weight distribution and presenting a gel permeation chromatogram shown by a broken line in Fig. 4, instead of 100 parts by weight of the copolymer used in Example 16.

Molecular-Weight Distribution:

1) Detection starting molecular weight (M_{START}): $2,9 \times 10^7$
2) Detection ending molecular weight (M_{END}): 245
3) Molecular weight of the maximum value P_H: 435000
4) Variance of the peak containing the maximum value P_H (M_W/M_N): 2,29
5) Area of the peak containing the maximum value P_H (S_H): 25
6) Molecular weight of the maximum value P_L: 13100
7) Variance of the peak containing the maximum value P_L (M_W/M_N): 2,32

8) Area of the peak containing the maximum value P_L (S_L): 75
9) Molecular weight of the minimum value V_M: 77000
10) Area of the valley containing the minimum value V_M (S_V): 18,8
11) Ratio (V/P): 0,188 .

Comparative Example 26

There was produced an electrophotographic toner having a volumetric median diameter of 11 μm in the same manner as in Example 16 except for the use of 100 parts by weight of a styrene (St)/methyl methacrylate (MMA)/butyl acrylate (BA) copolymer [St:MMA:BA = 80:7:13 (ratio by weight)] having the following molecular-weight distribution, instead of 100 parts by weight of the copolymer used in Example 16.

Molecular-Weight Distribution:

1) Detection starting molecular weight (M_{START}): $2,5 \times 10^7$
2) Detection ending molecular weight (M_{END}): 530
3) Molecular weight of the maximum value P_H: 600000
4) Variance of the peak containing the maximum value P_H (M_W/M_N): 2,2
5) Area of the peak containing the maximum value P_H (S_H): 32
6) Molecular weight of the maximum value P_L: 22000
7) Variance of the peak containing the maximum value P_L (M_W/M_N): 2,8
8) Area of the peak containing the maximum value P_L (S_L): 68
9) Molecular weight of the minimum value V_M: 85000
10) Area of the valley containing the minimum value V_M (S_V): 31,2
11) Ratio (V/P): 0,312 .

Comparative Example 27

There was produced an electrophotographic toner having a volumetric median diameter of 11 μm in the same manner as in Example 16 except for the use of 100 parts by weight of a styrene (St)/methyl methacrylate (MMA)/butyl acrylate (BA) copolymer [St:MMA:BA = 82:4:14 (ratio by weight)] having the following molecular-weight distribution, instead of 100 parts by weight of the copolymer used in Example 16.

Molecular-Weight Distribution:

1) Detection starting molecular weight (M_{START}): $4,0 \times 10^7$
2) Detection ending molecular weight (M_{END}): 390
3) Molecular weight of the maximum value P_H: 85000
4) Variance of the peak containing the maximum value P_H (M_W/M_N): 3,0
5) Area of the peak containing the maximum value P_H (S_H): 24
6) Molecular weight of the maximum value P_L: 5000
7) Variance of the peak containing the maximum value P_L (M_W/M_N): 2,3
8) Area of the peak containing the maximum value P_L (S_L): 76
9) Molecular weight of the minimum value V_M: 10800
10) Area of the valley containing the minimum value V_M (S_V): 29,5
11) Ratio (V/P): 0,295.

100 Parts by weight of the electrophotographic toner of each of Examples 16 to 18 and Comparative Examples 24 to 27 were mixed with 0,2 part by weight of hydrophobic silica to produce a mixture. Blended with the mixture was ferrite carrier having the average particle size of 80 μm. The resultant mixture was uniformly agitated and mixed to produce a two-component developer having toner density of 4,0%. The following tests were conducted on each of the developers thus obtained.

Image Density Preservation Test II

The image density preservation of each of the developers above-mentioned was evaluated in the same manner as in Image Density Preservation Test I except that a solid-black document was copied for 20 000

pieces under high-temperature and high-humidity conditions (35 °C and relative humidity of 85%) with each of two electrophotographic copying apparatus having different copying speeds [DC-3255 (copying speed of 432 pieces/minute) and DC-5585 (copying speed of 455 pieces/minute), both manufactured by Mita Industrial Co., Ltd.] using each of the developers above-mentioned.

Fog Test

A black-white document was copied for 20 000 pieces under high-temperature and high-humidity conditions (35 °C and relative humidity of 85%) with each of two electrophotographic copying apparatus having different copying speeds [DC-3255 (copying speed of 432 pieces/minute) and DC-5585 (copying speed of 455 pieces/minute), both manufactured by Mita Industrial Co., Ltd.] using each of the developers above-mentioned. By extracting every thousandth copied piece, total 21 copied pieces were extracted, as samples, from 20 000 copied pieces for each developer. With a reflection densitometer (TC-6D manufactured by Tokyo Denshoku Co., Ltd.), the density of the blank spaces of each sample was measured, and the number of samples of which image density was not greater than 0,003, was obtained. The developer with which there were obtained 20 or more samples, out of the total 21 samples, presenting an image density not greater than 0,003, was evaluated as excellent (O), the developer with which there were obtained 15 to 19 samples presenting an image density not greater than 0,003, was evaluated as good (Δ), and the developer with which there were obtained 14 or less samples presenting an image density not greater than 0,003, was evaluated as bad (X).

Image-Quality Uniformity Test II

The image-quality uniformity of each of the developers above-mentioned was evaluated in the same manner as in Image-Quality uniformity Test I except that a 20mm x 20mm solid-black document was copied with each of two electrophotographic copying apparatus having different copying speeds [DC-3255 (copying speed of 432 pieces/minute) and DC-5585 (copying speed of 455 pieces/minute), both manufactured by Mita Industrial Co., Ltd.] using each of the developers above-mentioned.

Blanking Test

A solid-black document was copied for 20 000 pieces under high-temperature and high-humidity conditions (35 °C and relative humidity of 85%) with each of two electrophotographic copying apparatus having different copying speeds [DC-3255 (copying speed of 432 pieces/minute) and DC-5585 (copying speed of 455 pieces/minute), both manufactured by Mita Industrial Co., Ltd.] using each of the developers above-mentioned. By extracting every thousandth copied piece, total 21 copied pieces were extracted, as samples, from 20 000 copied pieces for each developer. All the samples were visually checked for presence of blanking. The developer with which there were obtained 20 or more samples, out of the total 21 samples, presenting no blanking, was evaluated as excellent (O), the developer with which there were obtained 15 to 19 samples presenting no blanking, was evaluated as good (Δ), and the developer with which there were obtained 14 or less samples presenting no blanking, was evaluated as bad (X).

Together with the results of Fixing Property Test I, the results of the tests above-mentioned are shown in Table 4.

Table 4 (1/2)

	Copying Apparatus	Image Density Preservation	Fog	Image Quality Uniformity	Blanking
Example 16	DC-3255	O	O	O	O
	DC-5585	O	O	O	O
Example 17	DC-3255	O	O	O	O
	DC-5585	O	O	O	O
Example 18	DC-3255	O	O	O	O
	DC-5585	O	O	O	O
Comparative Example 24	DC-3255	O	O	Δ	O
	DC-5585	Δ	Δ	X	Δ
Comparative Example 25	DC-3255	O	O	O	Δ
	DC-5585	O	Δ	Δ	X
Comparative Example 26	DC-3255	O	O	Δ	O
	DC-5585	O	O	X	O
Comparative Example 27	DC-3255	O	O	Δ	O
	DC-5585	O	Δ	X	Δ

Table 4 (2/2)

	Fixing Property Test		
	F_1 (°C)	F_2 (°C)	FΔ (°C)
Example 16	140	195	55
Example 17	140	195	55
Example 18	135	190	55
Comparative Example 24	145	195	50
Comparative Example 25	140	195	55
Comparative Example 26	155	195	40
Comparative Example 27	135	175	40

From the results shown in Table 4, it was found that the electrophotographic toner of each of Examples 16 to 18 was excellent in fixing properties at a low temperature, and that the image formed with each of the toners above-mentioned was not decreased in density and the fixed image was good in quality without fog, coarseness, blanking and the like, with any of the two electrophotographic copying apparatus having different copying speeds.

As to the electrophotographic toner of each of Comparative Examples 24 to 27 which deviated in the molecular-weight distribution of the styrene/methyl methacrylate/butyl acrylate copolymer from the scope of the present invention, the resultant formed image was defective in any of the characteristics above-mentioned, particularly when the electrophotographic copying apparatus having a high copying speed (DC-5585) was used.

Further, the inside of the electrophotographic copying apparatus having a high copying speed (DC-5585) was checked after 20 000 copies had been taken with each of the toners above-mentioned. The apparatus presented no special problem when the toner of each of Examples 16 to 18 and Comparative Example 26 was used. However, when the toner of Comparative Example 24 was used, a great amount of fine powder resulting from pulverization of the toner was observed inside of the apparatus. Further, when the toner of Comparative Example 25 was used, a great amount of toner aggregate was found inside of the apparatus. When the toner of Comparative Example 27 was used, the fixing rollers of the apparatus were contaminated due to toner adhesion.

Claims

1. An electrophotographic toner containing
   (i) a fixing resin which is a styrene-acrylic copolymer presenting a gel permeation chromatogram of molecular-weight distribution in which the maximum value (PH, PL) appears in each of the ranges of not less than 1×10^5 and from 500 to 2×10^4, and
   (ii) a coloring agent which is carbon black having a dibutyl phthalate oil absorption of not less than 80ml/100g, the toner presenting a relaxation time of 10 to 50 ms at a frequency of 100 kHz.

2. The electrophotographic toner according to claim 1, wherein the styrene-acrylic copolymer has a molecular-weight distribution in which the minimum value (VM) appears between the two maximum values (PH, PL) and in which the ratio V/P of the total sum of two peak areas (SH, SL) respectively containing the two maximum values (PH, PL) to the area of the valley part (SV) containing the minimum value (VM) and located under a common tangential line (ℓ) which connects the two peaks (PH, PL) to each other, is not greater than 0,30.

3. An electrophotographic toner
   which contains, as a fixing resin, a styrene-acrylic copolymer presenting a gel permeation chromatogram of the molecular-weight distribution in which the maximum value (PH, PL) appears in each of the ranges of not less than 1×10^5 and from 500 to 2×10^4,
   and which presents a particle-size distribution in which the volumetric median diameter D_{50} as measured with a coulter counter is in a range from 7 to 13 μm and in which the ratio of particles having a particle size of not less than 16 μm is not greater than 0,90% in terms of the number of particles.

4. The electrophotographic toner according to claim 3, wherein the styrene-acrylic copolymer has a molecular-weight distribution in which the minimum value (VM) appears between the two maximum values (PH, PL) and in which the ratio V/P of the total sum of two peak areas (SH, SL) respectively containing the two maximum values (PH, PL) to the area of the valley part (SV) containing the minimum value (VM) and located under a common tangential line (ℓ) which connects the two peaks to each other, is not greater than 0,30.

5. An electrophotographic toner
   which contains, as a fixing resin, a styrene-acrylic copolymer having a gel permeation chromatogram of the molecular-weight distribution in which the maximum value (PH, PL) appears in each of the ranges of not less than 1×10^5 and from 500 to 2×10^4,
   and which presents a particle-size distribution in which the volumetric median diameter D_{50} as measured with a coulter counter is in a range from 7 to 13 μm and in which the ratio of a 75% residual particle size D_{75} to a 25% residual particle size D_{25} (D_{25}/D_{75}) is in a range from 1,3 to 1,7.

6. The electrophotographic toner according to claim 5, wherein the styrene-acrylic copolymer has a molecular-weight distribution in which the minimum value (VM) appears between the two maximum values (PH, PL) and in which the ratio (V/P) of the total sum of the two peak areas (SH, SL) respectively containing the two maximum values (PH, PL) to the area of the valley part (SV) containing the minimum value (VM) and located under a common tangential line (ℓ) which connects the two peaks (PH,PL) to each other, is not greater than 0,30.

7. An electrophotographic toner
containing, as a fixing resin, a styrene-acrylic copolymer presenting a gel permeation chromatogram of the molecular-weight distribution in which the maximum value (PH, PL) appears in each of the ranges of not less than 1×10^5 and from 500 to 2×10^4,
and in which a detection starting molecular weight corresponding to the upper limit of the molecular-weight distribution is not greater than 2×10^8 and a detection ending molecular weight corresponding to the lower limit of the molecular-weight distribution is not less than 300.

8. The electrophotographic toner according to claim 7, wherein the styrene-acrylic copolymer has a molecular-weight distribution in which the minimum value (VM) appears between two maximum values (PH, PL) and
in which the ratio (V/P) of the total sum of the two peak areas (SH, SL) respectively containing the two maximum values (PH, PL) to the area of the valley part (SV) containing the minimum value (VM) and located under a common tangential line (ℓ) which connects the two peaks (PH, PL) to each other, is not greater than 0,30.

Fig. 1

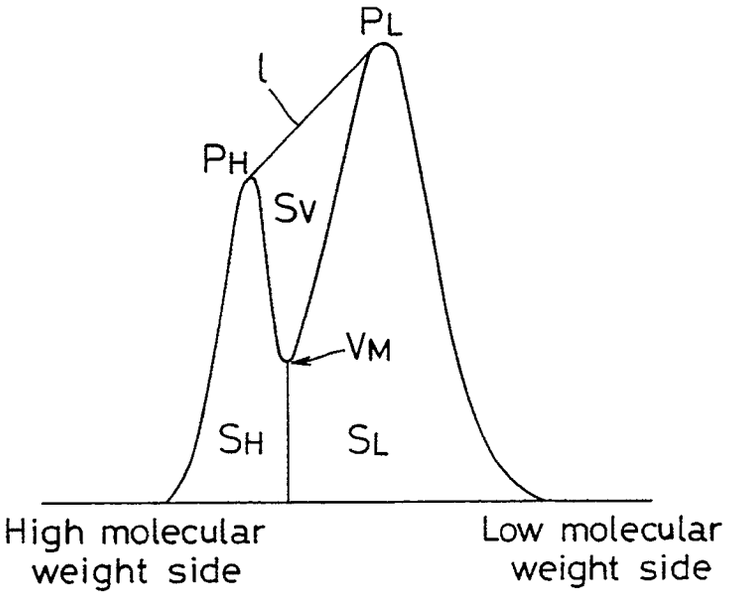

PL
l
PH
Sv
VM
SH
SL
High molecular weight side
Low molecular weight side

Fig. 2

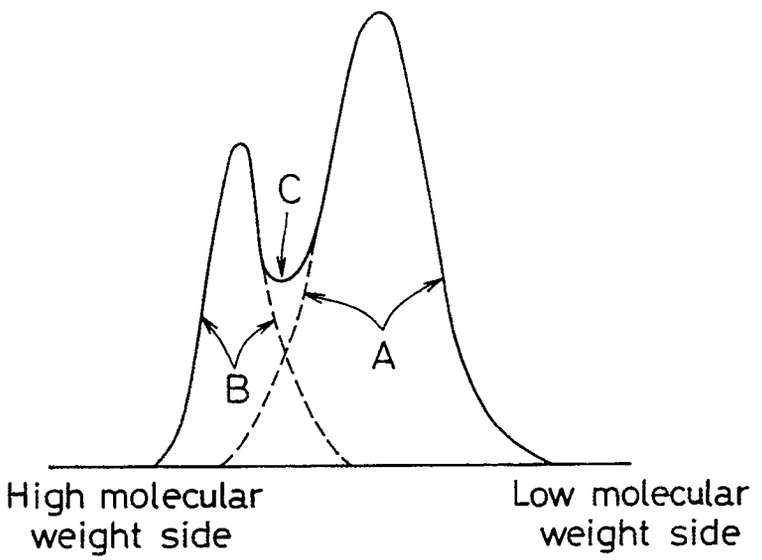

C
B
A
High molecular weight side
Low molecular weight side

Fig. 3

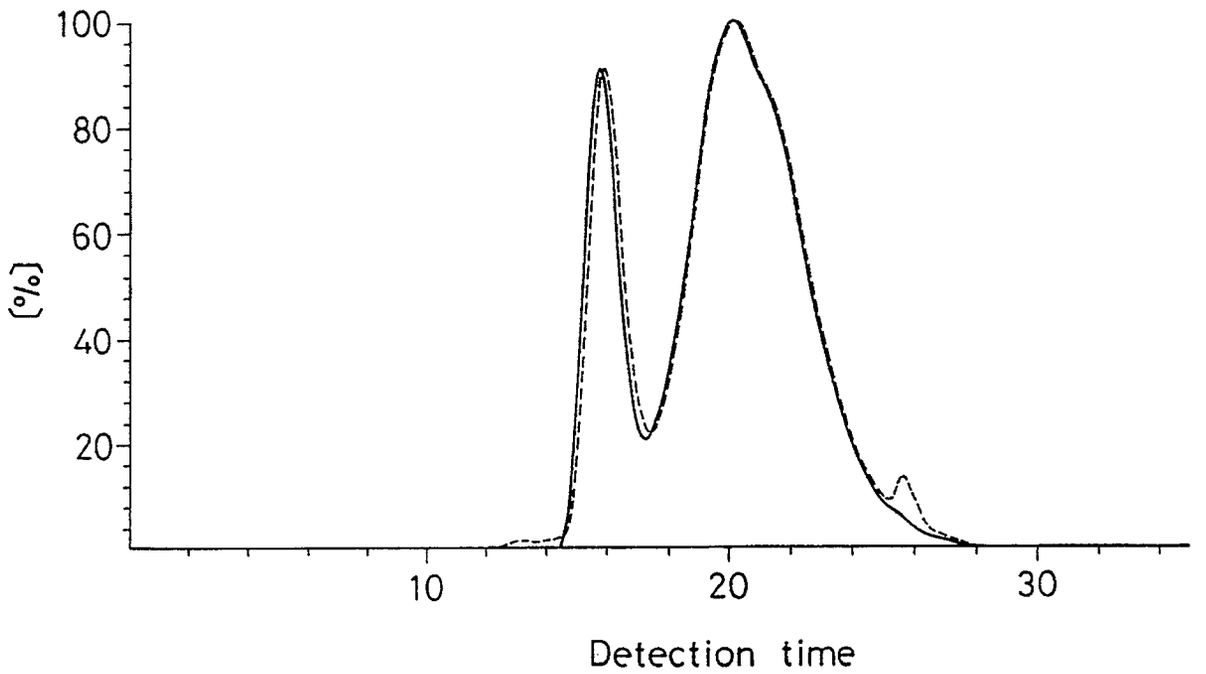
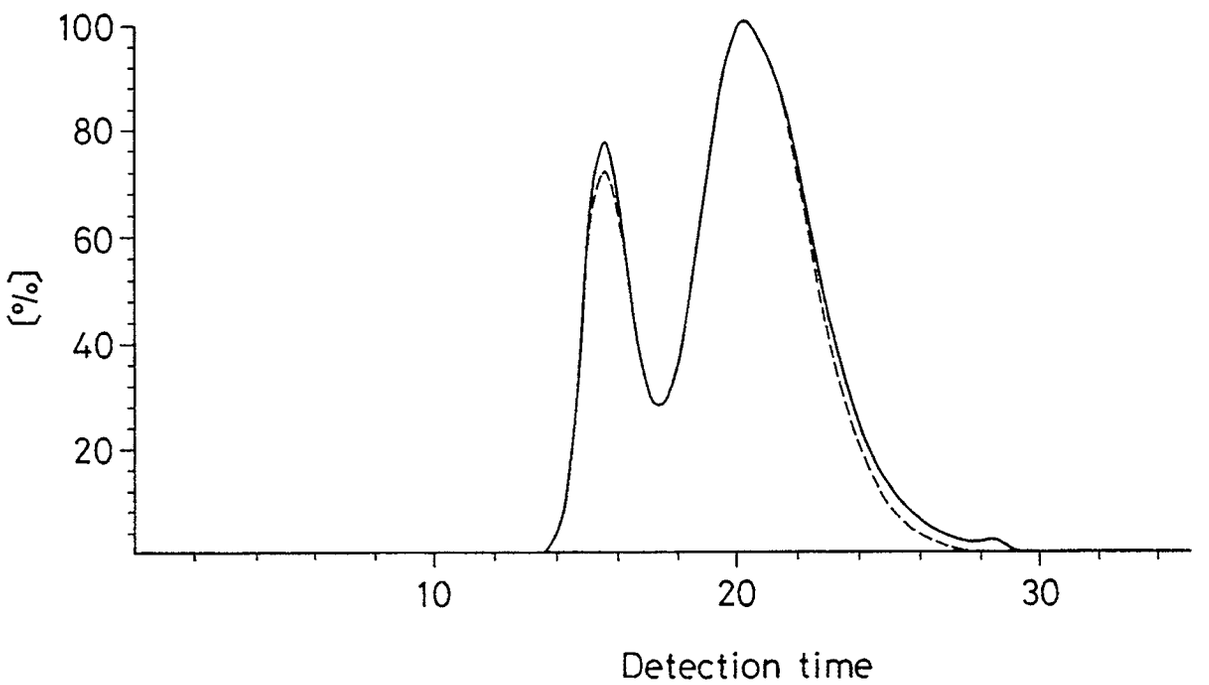


Fig. 4



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EUROPEAN SEARCH REPORT

Application Number

EP 91 10 5867

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)
A	EP-A-0 332 212 (MITA INDUSTRIAL CO., LTD.) * page 4, line 55 - page 5, line 22; claims 1-11 *	1-8	G 03 G 9/087 G 03 G 9/09
A	PATENT ABSTRACTS OF JAPAN vol. 14, no. 191 (P-1038)(4134) 18 April 1990, & JP-A-2 37365 (MITA INDUSTRIAL CO., LTD.) 07 February 1990, * the whole document *	1-8	
A	PATENT ABSTRACTS OF JAPAN vol. 13, no. 9 (P-811)(3357) 11 January 1989, & JP-A-63 217369 (KONICA CORP.) 09 September 1988, * the whole document *	1-8	

TECHNICAL FIELDS SEARCHED (Int. Cl.5)

G 03 G 9

The present search report has been drawn up for all claims

Place of search	Date of completion of search	Examiner
The Hague	22 July 91	HINDIAS E.

CATEGORY OF CITED DOCUMENTS

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