Description

FIELD OF THE INVENTION AND RELATED ART

This invention relates to a toner for developing electrostatic images in electrophotography, electrostatic recording, electrostatic printing, particularly to a toner for developing electrostatic images suitable for hot roller fixing obtained by a production process comprising pulverization, and further a binder resin for toner to be used in the toner, and a process for production of the resin.

In the prior art, a large number of electrophotographic processes have been known as described in U.S. Patent 2,297,691, Japanese Patent Publication Nos. 23910/1967 and 24748/1968. Generally speaking, in these processes, electrical latent images are formed on a photosensitive member of photoconductive substance by various means and subsequently developed by use of a toner, and the toner image is optionally transferred onto a transfer material such as paper, and then fixed by heating, pressurization, heating and pressurization, or with solvent vapor to obtain copied products. Then, the toner remaining on the photosensitive member without transfer is cleaned by various methods, and the above steps are repeated.

In recent years, such copying apparatus are not only used as copying machines for office works for copying original manuscripts generally referred to, but they are also beginning to be used in the field of printers as output means of computers or personal copiers for personal use.

Accordingly, further miniaturization, further reduction in weight and higher speed, higher reliability have been severely pursued, and the machines are becoming to be constituted of simpler elements in various respects. Consequently, the performances demanded for toner have become severer, and more excellent machines are not practically feasible unless improvement in performance of toner can be accomplished.

For example, various methods and devices have been developed concerging the steps of fixing toner images onto sheets such as paper, and the most general method currently available is the pressure heating system by hot rollers.

The pressure heating system performs fixing by permitting the toner image surface on the sheet to pass between the surfaces of not rollers having the surface formed of a material having release characteristic for the toner while under contact therewith under pressure. This method effects contact between the surfaces of the hot rollers and the toner image on the sheet for fixing under pressure, and therefore heat efficiency when the toner image sticks onto the sheet for fixing is very good, and fixing can be very rapidly effected so that it is very effectively applied to high speed electrophotographic copying machines. However, according to the above method, sine the hot roller surfaces come into contact with the toner images under pressure under molten state, a part of the toner images may be attached and transferred onto the fixing roller surfaces, and the attached toner is then retransferred onto the next sheet to be fixed, whereby the so-called offset phenomenon may sometimes occur to contaminate the sheet to be fixed. One of the essential conditions for the hot roller fixing system has been accepted to prevent the hot fixing roller surface from attachment of toner.

In the prior art, for the purpose of preventing attachment of toner onto the fixing roller surface, it has been practiced, for example, to form the roller surface of a silicone rubber or fluorine-containing resin which is the material excellent in release characteristic for toner, and further to cover its surface with a thin film of a liquid having good release characteristic such as silicone oil for preventing offset and preventing fatigue of the roller surface. However, although this method is very effective in preventing offset, since a device for feeding a liquid for prevention of offset is necessary, there is a problem that the fixing device becomes complicated.

This is in a direction opposite to the requirement of miniaturization and reduction in weight, and moreover silicone oil may be evaporated to contaminate internally the machine is some cases. Accordingly, based on the thought to feed an anti-offset agent from inside of the toner during heating without use of a device for feeding silicone oil, it has been proposed to add a release agent such as low molecular weight polyethylene, low molecular weight polypropylene. When a large amount of such additive is added for exhibiting sufficient effect, however, filming onto a photosensitive member or contamination of a toner-carrying member such as carrier particles or sleeve may occur to deteriorate images, posing a practical problem. Accordingly, it has been practiced to add a small amount of a release agent into toner, and to use in combination a slight amount of a releasable oil or a device for cleaning the offset toner of the wind-up system, for example, by use of a member such as web.

However, in view of the recent demands such as miniaturization, reduction in weight, and higher reliability, it is necessary or preferable to remove even these auxiliary equipments. Therefore, it is impossible to cope with these problems without further improvement in performances such as fixability and anti-offset characteristic of toner, which cannot be realized so easily unless the binder resin for toner is further improved. Concerning the technique for improvement of the binder resin for toner, for example, Japanese Patent Publication No. 23354/1976 proposes a toner by using a crosslinked polymer as the binder resin. While this method has

an effect of improving anti-offset characteristic and anti-winding characteristic, on the other hand, fixing point is elevated by increasing the degree of the crosslinking, and therefore no toner provided with sufficiently low fixing temperature, good anti-offset characteristic and anti-winding characteristic and sufficient fixability has not been obtained. Generally speaking, for improvement in fixability, the binder resin must be lowered in molecular weight to lower the softening point, which is antagonistic to the measure for improvement of anti-offset characteristic, and lowering in melting point will necessarily result in lowering in transition point of the resin, whereby undesirable phenomenon may also occur that the toner during storage suffers from blocking.

In contrast, Japanese Laid-Open Patent Appln. JP-A 56-158340 proposes a toner comprising a lower molecular weight polymer and a higher molecular weight polymer, but it is difficult to have this binder resin contain a crosslinking component and, for improving anti-offset characteristic to a higher performance, it is necessary to make the molecular weight of the higher molecular weight polymer, or increase its proportion. This approach leads to remarkably lower pulverizability, and it is difficult to obtain a practically satisfactory product. Further, concerning a toner comprising a low molecular weight polymer and a crosslinked polymer, for example, Japanese Laid-Open Patent Appln. JP-A 58-86558 proposes a toner comprising a lower molecular weight polymer and an infusible higher molecular weight polymer as the main resin components. According to this method, fixability and pulverizability tend to be improved, but because the weight-average molecular weight/number-average molecular weight (Mw/Mn) is as small as 3.5 or lower and the content of the insoluble and infusible higher molecular weight is so much as 40 to 90 wt.%, it is difficult to satisfy both of anti-offset characteristic and pulverizability, and practically it is extremely difficult to form a toner satisfying fixability (particularly, high speed fixing characteristic), anti-offset characteristic and pulverizability of the kneaded product for toner unless a fixer having a device for feeding a liquid for prevention of offset is used.

Further, if an insoluble and infusible higher molecular weight polymer is increased, the melt viscosity in thermal kneading during preparation of toner becomes very high, thermal kneading must be practiced at a temperature by far higher than in ordinary kneading, or at a high shear. Consequently, the former will result in lowering in toner characteristics by thermal deocmposition of other additives, while the latter will result in excessive cleavage of molecules of the binder resin, thus having a problem that the expected anti-offset performance cannot exhibited readily.

Japanese Laid-Open Patent Appln. JP-A 50-166958 proposes a toner comprising a resin composition component obtained by polymerization in the presence of a low molecular weight poly-α-methylstyrene with a number average molecular weight (Mn) of 500 to 1,500. Particularly, in the above Patent publication, it is stated that the number-average molecular weight (Mn) in the range of 9,000 to 30,000 is preferable, but if Mn is increased for further improvement in anti-offset characteristic, fixability and pulverizability during toner preparation pose problems and it is difficult to satisfy anti-offset characteristic and pulverizability during toner preparation at high levels. A toner prepared by use of a resin composition with poor pulverizability during toner preparation is lowered in production efficiency during toner preparation, and toner particles with coarse particle sizes are liable to be entrained, whereby it may sometimes give undesirably scattered images in respect of a toner performance.

Japanese Laid-Open Patent Appln. JP-A 56-16144 (corres. to U.S. Patent No. 4499168) proposes a toner containing a binder resin component having at least one maximum value in the regions of molecular weights of 10^3 to 8×10^4 and 10^5 to 2×10^6, respectively, in the molecular weight distribution obtained by GPC (gel permeation chromatography). In this case, although pulverizability, anti-offset characteristic, anti-filming or anti-sticking onto a photosensitive member and image quality are excellent, further improvement in anti-offset characteristic and fixability is demanded. Particularly, it is difficult for to this resin maintain various other performances with further improvement in fixability, or respond to the severe requirements of today while improving such performances.

Thus, it is extremely difficult to realize both fixing characteristic and pulverizability at high levels. Particularly, pulverizability of the kneaded product during toner preparation is an important factor in the trend of today to make smaller the particle size of toner from the demands of giving higher quality copied image, higher resolution and higher fine line reproducibility. Further, since the pulverization step requires enormous energy, improvement in pulverizability is also important in aspect of conservation of energy.

Sticking of toner onto inner walls of a pulverizing device is liable to be generated in a toner with good fixability, whereby pulverization efficiency becomes worse. Further, as another aspect, it is also necessary to pay attention to step of cleaning the toner remaining on the photosensitive member after transfer in other copying steps. Today, cleaning with blade (blade cleaning) is generally practiced in view of miniaturization, reduction in weight, and reliability. Along with prolonged life of photosensitive member, miniaturization of photo-sensitive drum, etc. and acceleration of speed of the system, anti-sticking and anti-filming characteristic onto a photosensitive member demanded for toner are becoming more severe. Particularly, amorphous silicon photosensitive members which have been practically applied recently are highly durable, and also OPC (organic pho-

toconductor) is elongated in life, and accordingly various performances demanded for toner are becoming higher.

Miniaturization of a copying machine or a printer must be done by housing the respective elements in a narrow space. For this purpose, the space where air is allowed to pass becomes smaller, and also the fixer and heating source of exposure system are placed very close to the toner hopper and cleaner, whereby the toner is exposed to a high temperature atmosphere. Accordingly, a toner cannot be practically applied unless it has a further improved anti-blocking characteristic.

In view of examples as described above, requirements for a toner are severe, but the demands cannot be satisfied unless these can be improved at the same time. However, it is not meaningful at all to realize these, if image quality, durability of toner, developing characteristic, further production efficiency are lowered thereby.

These performances are greatly attributable to primarily the performances of the binder resin for toner. Although there are proposals to improve these by use of additives of release agents, plasticizers and others, but these are subsidiary.

As shown in Figure 7 of the accompanying drawing, various performances required for toner are antagonistic to each other in most cases, and yet it has been increasingly demanded to satisfy all of them at high levels.

SUMMARY OF THE INVENTION

An object of the present invention is to provide a toner which has solved the problems as described above.

Another object of the present invention is to provide a toner suitable for hot roller fixing system free from application of an oil.

Still another object of the present invention is to provide a toner which can be fixed at a low temperature and also is excellent in anti-offset characteristic.

Still another object of the present invention is to provide a toner which can be fixed at a low temperature and yet will not generate sticking or filming onto a photosensitive member even in a high speed system and use for a long term.

Still another object of the present invention is to provide a toner which can be fixed at low temperature, and yet is excellent in anti-blocking characteristic and particularly sufficiently useful in a high temperature atmosphere in a small machine.

Still another object of the present invention is to provide a toner which can be fixed at a low temperature and yet can be produced continuously with good efficiency due to no sticking of the pulverized product onto the inner walls of a pulverizing device in the pulverizing step during manufacture of the toner.

Still another object of the present invention is to provide a toner which is excellent in anti-offset characteristic and can be produced with good efficiency due to excellent pulverizability.

Still another object of the present invention is to provide a toner which is excellent in anti-offset characteristic, contains no more resin components insoluble in tetrahydrofuran (THF) than is necessary, and will not be denaturated or deteriorated in the thermal kneading step of toner.

Still another object of the present invention is to provide a toner which is little in amount of coarse powder due to good pulverizability and therefore little in scattering of powder around image, and can form stable and good developed images.

Still another object of the present invention is to provide a binder resin for toner excellent in anti-sticking characteristic within the device during pulverization or anti-sticking characteristic onto a photosensitive member, and a process for production thereof.

Still another object of the present invention is to provide a binder for toner without any problem in developability, particularly image quality and durability, and a process for production thereof.

Still another object of the present invention is to provide a binder for toner satisfying excellent performances in various items at the same time, and a process for production thereof.

Still another object of the present invention is to provide a binder for toner which is excellent in fixing characteristic, and at the same in anti-offset characteristic, anti-winding characteristic and anti-blocking characteristic, and a process for production thereof.

Still another object of the present invention is to provide a binder for toner which is good in pulverizability and also good in production efficiency of toner, and a process for production thereof.

According to the present invention, there is provided a toner for developing an electrostatic latent image, comprising a colorant or magnetic powder and a binder resin, said binder resin having 10 to 60 wt.% of a chloroform-insoluble or THF (tetrahydrofuran)-insoluble and 40 to 90 wt.% of a chloroform-soluble or THF-soluble and comprising 10 to 50 wt.% of components having molecular weights of 10,000 or less, the chloroform-solu-

ble or THF-soluble having a molecular weight distribution in the chromatogram of GPC (gel permeation chromatography) thereof such that it provides a ratio (Mw/Mn) of weight-average molecular weight (Mw)/number-average molecular weight (Mn) ≧ 5, and there are at least one peak in the molecular weight range of 2,000 to 10,000 and at least one peak or shoulder in the range of 15,000 to 100,000.

Preferred embodiments of the toner according to the present invention are set out in the sub claims to claim 1.

According to another aspect of the present invention, there is provided a process for production of a binder resin, which comprises forming a polymer having a molecular weight distribution by GPC such that it has the main peak in the region of molecular weights 2,000 - 10,000 and a ratio of weight average molecular weight/number average molecular weight (Mw/Mn) ≦ 3.5 and Tg ≧ 50°C by solution polymerization and carrying out suspension polymerization reaction by dissolving said polymer in a polymerizable monomer to prepare a resin composition containing 10 to 70 wt.% of chloroform- or THF-insoluble, and the chloroform- or THF-soluble having a molecular weight distribution such that it has a ratio Mw/Mn ≧ 5, and at least one peak in the region of molecular weights 2,000 - 10,000, at least one peak or shoulder in the region of molecular weights 15,000 - 100,000 and the components of molecular weights of 10,000 or less at a ratio of 10 to 50 wt.% based on the whole resin.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 shows a GPC chromatogram of the THF-soluble of the toner of Example 1;
Figure 2 shows a GPC chromatogram of the THF-soluble of the resin of Synthesis Example 1;
Figure 3 shows a GPC chromatogram of THF-soluble of the polystyrene obtained in polymerization in the first step in Synthesis Example 1;
Figure 4 shows a GPC chromatogram of THF-soluble of the copolymer obtained when the styrene-n-butyl acrylate copolymer in Synthesis Example 1 was suspension polymerized alone;
Figure 5 is a combined chart of the chart in Figure 3 and the chart in Figure 4;
Figure 6 is a chart prepared by overlapping the chart in Figure 2 (solid line) with the chart in Figure 5 (broken line) for comparative purpose;
Figure 7 is a diagram showing correlations between the respective characteristics demanded for the toner;
Figure 8 shows a graph showing the relation-ship between the content of THF-insoluble and pulverizability;
Figure 9 shows a graph concerning the relationship between the content of the components of molecular weights of 10,000 or less and the toner characteristics;
Figure 10 shows a chromatogram of the THF-soluble of the resin composition-7;
Figure 11 shows a chromatogram of the THF-soluble of the binder resin used in Comparative Example 9; and
Figure 12 shows a chart of GPC of the THF-soluble of the resin composition prepared in Example 15.

DETAILED DESCRIPTION OF THE INVENTION

In order to accomplish the objects as mentioned above at the same time, we have made an intensive study on compositions and performances of various binder resins from various viewpoints. As a consequence, it has been found that the above mentioned objects can be accomplished when the proportion of the THF-insoluble in the binder resin and the molecular distribution of THF-soluble satisfy specified conditions. When a binder resin is dissolved in a solvent such as chloroform or THF, it can be separated into an insoluble and a soluble, and the soluble can be subjected to measurement of the molecular weight distribution by GPC (gel permeation chromatography). To attract attention on the amount of THF-insouble and the position of the main peak of the molecular weight distribution of THF-solubles, there is a relationship between the position and pulverizability as shown in Figure 8. As a result, it can be seen that a system with no or little THF-insoluble is very disadvantageous, thus supporting the fact as mentioned above that the shifting of the position of the peak in the molecular weight distribution simply toward the position of lower molecular weight for the purpose of improving pulverizability will worsen anti-offset characteristic, whereby it is difficult to satisfy anti-offset characteristic and pulverizability in combination.

From this investigation, it has been found that it is very effective to incorporate a specific amount of THF-insoluble not only for the purpose of improving anti-offset characteristic as conventionally considered but also for the purpose of improving pulverizability during preparation of toner.

Further, the molecular weight distribution of THF-soluble and the property as to whether the fixable temperature is high or low (hereinafter merely referred to as fixability), anti-offset characteristic, pulverizability and anti-blocking characteristic were investigated. As a result, for example, as shown in Figure 9, it has been

found that the components having molecular weights of about 10,000 or less and 10,000 or more in the GPC molecular weight distribution have different functions. It has been found that the proportion of the components having molecular weight of 10,000 or less based on the total binder resin will not remarkably influence fixability or anti-offset characteristic contrary to that conventionally mentioned, but it is substantially irrelevant if it is in a specific range above a certain value, and instead it strongly relates to pulverizability.

Further, from other investigations, it has been also found that in a binder resin system, the THF-insoluble influences primarily anti-offset characteristic, anti-winding characteristic and pulverizability basically, and that the components of molecular weights of 10,000 or less of THF-soluble influence primarily pulverizability, anti-blocking characteristic, anti-sticking or anti-filming characteristic onto a photosensitive member and sticking onto the inner walls of a pulverizer, and further that the amount of the components of molecular weights of 10,000 or more of THF-soluble influence primarily fixability. As a result, the proportion of the components of molecular weights of 10,000 or less is 10 to 50 wt.%, preferably 10 to 39 wt.%. For exhibiting sufficient performances, it is further required that the distribution has a peak in the region of molecular weight of 2,000 to 10,000 (preferably 2,000 - 8,000) and a peak or a shoulder in the region of molecular weight of 15,000 to 100,000 (preferably 20,000 - 70,000). If there is no peak in the range of 2000 -10000 and there is a peak at 2,000 or less, but the proportion of the components of molecular weight 10,000 or less is 50 wt.% or more, some problems may be caused in anti-blocking characteristic, anti-sticking or anti-filming characteristic onto a photosensitive member, or sticking onto inner walls of a pulverizer. If there is no peak at 10,000 or less, and there is a peak at 10,000 or more while the proportion of the components of molecular weight 10,000 or less is 10 wt.% or less, there is posed a problem particularly with respect to pulverizability, and also formation of coarse particles may pose a problem.

If there is no peak or shoulder in the region of molecular weight 15,000 or more and there is only a peak in the region of molecular weight 15,000 or less, anti-offset characteristic will pose a problem. If there is no peak or shoulder in the region of molecular weight 15,000 - 100,000, and there is the main peak at 100,000 or higher, pulverizability will pose a problem.

Further, the THF-soluble is required to satisfy the relationship of $Mw/Mn \geqq 5$, and if Mw/Mn is lower than 5, anti-offset characteristic tends to be lowered and problematic.

Preferably, Mw/Mn may be 80 or less, more preferably satisfy the relation of $10 \leqq Mw/Mn \leqq 60$.

Particularly, when Mw/Mn is $10 \leqq Mw/Mn \leqq 60$, especially excellent performances can be exhibited in various characteristics such as pulverizability, fixability, anti-offset characteristic, image quality, etc.

Here, Mw is weight-average molecular weight measured by GPC as described below, and Mn is number-average molecular weight by the same measurement.

The content of chloroform-insoluble or THF-insoluble in the binder resin for toner is 10 to 60 wt.%. If it is less than 10 wt.%, anti-offset characteristic becomes a problem, while at a content over 60 wt.%, thermal fixing temperature tends to be elevated.

More preferably, the content of chloroform-insoluble THF-insoluble may be 10 to 50 wt.%. Further preferably, the range of 15 to 49 wt.% is preferable in view of pulverizability and anti-offset characteristic.

The content of chloroform-insoluble or THF-insoluble is required to be controlled in view of the THF-soluble content, the peak position in GPC chromatogram of THF-soluble and cleavage of polymer molecular chains during thermal kneading.

In the process according to the invention, the proportion of THF-insoluble in the resin for toner is 10 to 70 wt.% (particularly 10 to 60 wt.%). If THF-insoluble is less than 10 wt.%, anti-offset characteristic and anti-winding characteristic may become problematic, while at higher than 70 wt.%, the problem of deterioration due to cleavage of molecular chains during thermal kneading for preparation of toner may occur. Preferably, the range of 15 to 59 wt.% (more preferably 1t to 49.%) may be used.

When the glass transition point Tg_1 of the resin of the molecular weight components of 10,000 or less in the THF-soluble is compared with the Tg_t of the whole resin, if the relationship of $(Tg_1) \geqq (Tg_t - 5)$ is satisfied, fixability, pulverizability, anti-sticking, anti-filming characteristic onto a photosensitive member, inhibition of sticking on inner walls of a pulverizer, and anti-blocking characteristic will become better.

Tg_1 as herein mentioned is measured by the following method. Under THF flow at a rate of 7 ml/min. at 25°C, a sample solution in THF with a concentration of about 3 mg/ml of THF-soluble in toner is injected in an amount of about 3 ml into a molecular weight distribution measuring apparatus, and the components of molecular weights of 10,000 or less are separated and collected. After collection, the solvent is evaporated under reduced pressure and further dried in an atmosphere of 90°C under reduced pressure for 24 hours. The above operation is repeated until about 20 mg of the components with molecular weights of 10,000 or less is obtained. The obtained sample is subjected to annealing at 50°C for 48 hours, and thereafter Tg is measured by differential scanning calorimetry, and the measured value is defined as Tg_1.

As the column for separation, TSKgel, G2000H, TSKgel G2500H, TSKgel G3000H, TSKgel G4000H (pro-

duced by Toyo Soda Kogyo K.K.) may be employed, but in the Examples of the present invention described hereinafter, TSKgel G2000H and TSKgel G3000H were employed in combination.

The value of Tg_t which is the Tg of a toner is determined by differential scanning calorimetry after subjecting the toner to annealing at 50°C for 48 hours.

According to a most preferred embodiment of the present invention, there is provided a toner containing a binder resin, having a ratio of h_1/h_2 of 0.4/1 to 4.0/1, when the height of the highest peak in the region of molecular weight of 15,000 to 100,000 is denoted by h_2 and the height of the highest peak in the region of molecular weight of 2,000 to 10,000 is denoted by h_1 in the GPC molecular weight distribution of THF-soluble, as shown in Figure 1. Further, the number-average molecular weight of THF-soluble may be preferably $2,000 \leq Mn \leq 9,000$. If $Mn < 2,000$, anti-offset characteristic becomes problematic, while if $9,000 < Mn$, pulverizability and fixability will become problematic.

The chloroform-insoluble (gel component) or THF-insoluble in the present invention represents a weight ratio of the polymer components (substantially crosslinked polymer) which have become insoluble in chloroform or THF solvent in the resin composition in the toner, and can be used as a parameter indicating the extent of crosslinking of a resin composition containing crosslinked components. The chloroform-insoluble or THF-insoluble is defined by the value measured as described below.

A toner sample is weighed in an amount of 0.5 to 1.0 g (W_1 g), placed in a cylindrical filter paper (e.g. No. 86 R, produced by Toyo Roshi K.K.) and subjected to a Soxhlet's extractor to effect extraction with the use of 100 to 200 ml of chloroform or THF as the solvent for 6 hours. The soluble extracted with the solvent is subjected to evaporation, and then vacuum-dried at 100°C for several hours, and the amount of the chloroform- or THF-soluble resin component is weighed (W_2 g). The weight of the components other the resin component such as magnetic material or pigment in the toner is defined as (W_3 g). The chloroform- or THF-insoluble is defined from the following formula:

$$\text{Chloroform- or THF-insoluble (\%)} = \frac{W1 - (W3 + W2)}{(W1 - W3)} \times 100$$

In the present invention, the molecular weight of a peak or/and a shoulder in a chromatogram by GPC (gel permeation chromatography), may be measured under the following conditions.

Through a column stabilized in a heat chamber at 40°C, THF (tetrahydrofuran) as the solvent is permitted to flow at a rate of 1 ml/min., and 50 to 200 µl of a THF sample solution of a resin controlled to a sample concentration of 0.05 to 0.6 wt.% is injected for measurement. In measuring the molecular weight of the sample, the molecular weight distribution possessed by the sample is calculated based on a calibration curve prepared from several kinds of mono-dispersed polystyrene standard samples showing a relationship between the logarithmic value of the molecular weights and the count numbers. As the standard polystyrene samples for preparation of the calibration curve, for example, those produced by Pressure Chemical Co. or Toyo Soda Kogyo K.K., having molecular weights of $6x10^2$, $2.1x10^3$, $4x10^3$, $1.75x10^4$, $5.1x10^4$, $1.1x10^5$, $3.9x10^5$, $8.6x10^5$, $2x10^6$, $4.48x10^6$ may be employed, and it is suitable to use at least 10 points of standard polystyrene samples. As the detector, an RI (refractive index) detector is used.

As the column, for measuring adequately a molecular region of 10^3 - $2x10^6$, a plurality of commercially available polystyrene gel columns may be preferably combined. For example, a combination of µ-styragel 500, 10^3, 10^4 and 10^5 produced by Waters Co., a combination of Shodex KF-80M, KF-802, 803, 804 and 805 produced by Showa Denko K.K., or a combination of TSKgel G1000H, G2000H, G2500H, G3000H, G4000H, G5000H, G6000H, G7000H and GMD produced by Toyo Soda K.K., are preferred.

The weight % of the components of molecular weights 10,000 or lower relative to the binder resin is determined by cutting out the portion of chromatogram corresponding to the components of molecular weights of 10,000 or less, calculating the weight ratio relative to the portion of chromatogram cut out corresponding to the components of 10,000 or more, and calculating the weight % relative to the whole resin by use of the weight % of the above THF insoluble.

The above binder resin characterized by the parameters may occupy 60 wt.% or more, preferably 80 wt.% or more, particularly preferably 90 wt.% or more of the total amount of binder resin in the toner of the present invention.

Further, in the above molecular weight distribution of GPC, when the chromatogram is divided into three portions with the molecular weights $3x10^4$ and $50x10^4$ as the boundaries, namely into a component A (region of $50x10^4$ or higher), a component B (region of $3x10^4$ to $50x10^4$) and a component C (region of $3x10^4$ or lower), respectively, from the higher molecular weight side, and the constituent ratios of the respective regions relative to the whole chromatogram are determined from integrated values of the chromatogram or by the weight from the respective weights of the chromatogram cut out into three portions, the constituent ratios may be 0 to 20 %, preferably 0 to 15 %, more preferably 0 to 10 %, furthermore preferably 1 - 9 %, for the component A; 10 to 60 %, preferably 15 to 55 %, more preferably 20 to 50 % for the component B; and 20 to 90 %, preferably

35 to 80 %, more preferably 40 to 70 % for the component C.

The reason for these is because, in a relationship between the chloroform- or THF-soluble and the chloroform- or THF-insoluble, a resin composition with a gel component of 60 % or higher will bring about elevation in fixing temperature and further invite poor dispersibility of the additive when used for toner, due to the melting characteristic of the crosslinked components. Further, cleavage of the highly crosslinked components will readily occur during kneading of the resin, thereby causing troubles in designing of toner. When the gel component is less than 0.1 %, offset, winding around rollers will readily occur, and further when the gel component is less than 0.1 % and the content of the higher molecular region is high, pulverizability will be remarkably worsened.

If the molecular weights of the solvent soluble have no main peak value in the range of 1,000 to 25,000, and the main peak value is at 25,000 or higher, the fixing temperature of the toner prepared will be elevated to narrow the fixing temperature region, and also the pulverizability is worsened to bring about lowering in production efficiency. If the molecular weight of the main peak value is lower than 1,000, the toner prepared will be remarkably worsened in anti-offset characteristic or anti-winding characteristic around rollers, and further a problem may sometimes occur in blocking. If there is no sub-peak or sub-shoulder in the molecular weight range of 3,000 to 150,000, and their values are higher than 150,000, dispersibility of additive is poor, and also fixing temperature is remarkably elevated, with pulverizability being further remarkably worsened. If the molecular weight for a sub-peak or sub-shoulder is less than 3,000, the toner prepared is worsened in anti-offset characteristic, anti-winding characteristic around rollers, and further a problem may sometimes occur in blocking. In the toner of the present invention, the above problems are markedly improved, and a toner with excellent anti-offset characteristic, anti-winding characteristic around rollers, broad fixing temperature region and yet with excellent developing characteristics and good pulverizability can be obtained.

It is further preferred that the binder resin contains 10 - 50 wt.% of the chloroform-insoluble, and the THF-soluble of the binder resin has, in the GPC chromatogram thereof, a main peak in the molecular weight range of 2,000 to 15,000 and a sub-peak or shoulder in the molecular weight range of 8,000 to 80,000.

The resin composition in the toner of the present invention may be preferably polymers or copolymers obtained by polymerization of at least one monomer selected from styrene type monomers, acrylic acid type monomers, methacrylic acid type monomers and derivatives thereof for developing characteristics and charging characteristics. Examples of the monomers may include styrene type monomers such as styrene, α-methylstyrene, vinyltoluene, chlorostyrene and the like; acrylic acid type monomers, methacrylic acid type monomers and derivatives thereof such as acrylic acid, methyl acrylate, ethyl acrylate, propyl acrylate, butyl acrylate, octyl acrylate, 2-ethylhexyl acrylate, n-tetradecyl acrylate, r-hexadecyl acrylate, lauryl acrylate, cyclohexyl acrylate, diethylaminoethyl acrylate, dimethylaminoethyl acrylate and other acrylates, similarly methacrylic acid and methacrylates such as methyl methacrylate, ethyl methacrylate, propyl methacrylate, butyl methacrylate, amyl methacrylate, hexyl methacrylate, 2-ethylhexyl methacrylate, octyl methacrylate, decyl methacrylate, dodecyl methacrylate, lauryl methacrylate, cyclohexyl methacrylate, phenyl methacrylate, 2-hydroxyethyl methacrylate, 2-hydroxypropyl methacrylate, dimethylaminoethyl methacrylate, glycidyl methacrylate, stearyl methacrylate and the like. Other than the monomers as mentioned above, a small amount of other monomers within the range which can accomplish the objects of the present invention may be employed, such as acrylonitrile, 2-vinylpyridine, 4-vinylpyridine, vinyl carbazole, vinyl methyl ether, butadiene, isoprene, maleic anhydride, maleic acid, maleic acid monoesters, maleic acid diesters, vinyl acetate.

As the crosslinking agent to be used in the toner of the present invention, there may be included as a bifunctional crosslinking agent, divinylbenzene, bis(4-acryloxypolyethoxyphenyl)propane, ethylene glycol diacrylate, 1,3-butylene glycol diacrylate, 1,4-butanediol diacrylate, 1,5-pentanediol diacrylate, 1,6-hexanediol diacrylate, neopentyl glycol diacrylate, diethylene glycol diacrylate, triethylene glycol diacrylate, tetraethylene glycol diacrylate, respective diacrylates of polyethylene glycol #200, #400, #600, dipropylene glycol diacrylate, polypropylene glycol diacrylate, polyester type diacrylate (MANDA, Nippon Kayaku, K.K.), and methacrylates corresponding to the above acrylates.

Examples of polyfunctional crosslinking agent may include pentaerythritol acrylate, trimethylolethane triacrylate, trimethylolpropane triacrylate, tetramethylolmethane tetraacrylate, oligoester acrylate, and corresponding methacrylates, 2,2-bis(4-methacryloxy-polyethoxyphenyl)propane, diallyl phthalate, triallyl cyanurate, triallylazo cyanurate, triallyl isocyanurate, triallyl trimellitate, and diallyl chlorendate.

The method for synthesizing the binder resin according to the present invention may be preferably a method in which two or more kinds of polymers are synthesized.

In a method for preparing the binder resin of the present invention, a first resin is prepared by solution polymerization, the first resin is dissolved in a polymerizable monomer and the polymerizable monomer is suspension polymerized in the presence of the first resin and a crosslinking agent. It is preferable to dissolve 10 to 120 parts by weight, preferably 20 to 100 parts by weight of the first resin per 100 parts by weight of the monomer for suspension polymerization. During the suspension polymerization, it is preferable to use about

0.1 to 2.0 wt.% of a crosslinking agent based on the monomer to be suspension-polymerized. Slight change in these conditions may be tolerable depending on the kind of initiator and the reaction temperature.

It has been found that a binder resin obtained by dissolving a first polymer in a monomer followed by suspension polymerization of the monomer is different from a blended polymer obtained by mere mixing of the first polymer and a polymer obtained by suspension polymerization of the monomer without dissolving the first polymer.

The difference resides in the point that the former is slightly richer in high molecular weight components in the chromatogram of GPC of THF-soluble than the latter, giving a broader molecular weight distribution. The former comprises molecular weights of 30×10^4 or more at a ratio of 3 to 25 wt.% of the whole resin, which is clearly greater than that of the latter. This may be attributable to the fact that the first polymer dissolved influences suspension polymerization, which provides an advantageous effect not attainable by homogeneous mixing of the polymers. This is described in more detail by referring to the GPC charts shown in the accompanying drawings.

Figure 2 in the accompanying drawings shows a chart of GPC of a resin composition obtained in Synthesis Example 1 as described below. Figure 3 shows a chart of GPC of a polystyrene prepared in solution polymerization which is a first polymerization. The polystyrene was soluble in THF, and also soluble in styrene monomer and n-butyl acrylate monomer which were polymerization monomers, and had a main peak at a molecular weight of 3,500. Figure 4 shows a chart of GPC of THF-soluble of the product formed by suspension polymerization of a styrene-n-butyl acrylate copolymer prepared in the second polymerization under the same conditions except that the polystyrene was not added. The styrene-n-butyl acrylate copolymer was found to have a main peak at a molecular weight of 40,000.

Figure 5 is a combination of the chart in Figure 3 and the chart in Figure 4.

Figure 6 shows a superposition of the chart in Figure 2 and the chart in Figure 5 (converted into a line). As is also apparent from Figure 6, the resin composition obtained in Synthesis Example 1 according to the present invention was found to have a GPC chart which was different from that of the product obtained by merely mixing the polystyrene and the styrene-n-butyl acrylate copolymer separately polymerized. Particularly, on the higher molecular side, a polymer component not formed in the styrene-n-butyl acrylate copolymer alone is found to be formed. This higher molecular weight component may be considered to be formed by the presence of the polystyrene prepared in the first step solution polymerization during the suspension polymerization which is the second step polymerization, with the polystyrene functioning as the polymerization controller, whereby synthesis of THF-insoluble and THF-soluble of styrene-n-butyl acrylate copolymer is controlled. In the resin composition according to the present invention, THF-insoluble, high molecular components soluble in THF, intermediate molecular weight components soluble in THF and low molecular weight components soluble in THF, are homogeneously mixed. Further, the resin composition according to the present invention has an ability of forming a new peak in the region of the molecular weights of 30×10^4 or higher (preferably 50×10^4 or higher) through cleavage of molecular chains in the melting and kneading step during preparation of toner, to control fixability and anti-offset characteristic of the toner.

Further, in the present invention, it is preferable that the components of molecular weights of 30×10^4 or more is contained in an amount of 5 to 30 wt.% (preferably 10 to 30 wt.%) of the binder resin based on GPC of THF-soluble in the toner. In GPC of THF-soluble in toner, a binder resin having a clear peak at molecular weights of 30×10^4 or higher (preferably 50×10^4 or higher) is more preferable with respect to improvement in anti-offset characteristic and anti-winding characteristic.

The solution polymerization process and the suspension polymerization process according to the present invention are described below.

As the solvent to be used in the solution polymerization, xylene, toluene, cumene, cellulose acetate, isopropyl alcohol, benzene, etc. may be employed. In the case of a styrene monomer, xylene, toluene or cumene is preferred. It may be suitably selected depending on the polymer formed. The initiator may include di-tert-butylperoxide, tertbutyl peroxybenzoate, benzoyl peroxide, 2,2'-azobisisobutyronitrile, 2,2'-azobis(2,4-dimethylvalelonitrile), etc., which may be used at a concentration of 0.1 part by weight or more (preferably 0.4 to 15 parts by weight) based on 100 parts by weight of the monomer. The reaction temperature, which may depend on the solvent, the initiator employed and the polymer to be polymerized, may be preferably 70°C to 180°C. In the solution polymerization, it is preferable to use 30 parts to 400 parts by weight of the monomer per 100 parts by weight of the solvent.

In the suspension polymerization, it is preferable to use 100 parts by weight or less (preferably 10 to 90 parts by weight) of the monomer per 100 parts by weight of an aqueous dispersion medium. Available dispersing agents may include polyvinyl alcohol, partially saponified polyvinyl alcohol, calcium phosphate, etc., and may be used in an amount of 0.05 to 1 part by weight based on 100 parts by weight of the aqueous dispersion medium as an appropriate amount while it may somewhat depends on the amount of the monomer relative to

the aqueous dispersion medium. The polymerization temperature may be appropriately 50 to 95°C, and it should be selected suitably depending on the initiator employed and the desired polymer. Also, although any kind of initiator can be used so long as it is insoluble or hardly soluble in water, for example, benzoyl peroxide, tert-butylperoxy hexanoate, etc., may be used in an amount of 0.5 to 10 parts by weight based on 100 parts by weight of the monomer.

In the toner using the resin of the present invention, in addition to the above binder resin component, the following components may be incorporated at a ratio smaller than the content of said binder resin component, within the range which does not adeversely affect the effect of the present invention.

For example, there may be added silicone resin, polyester, polyurethane, polyamide, epoxy resin, polyvinyl butyral, rosin, modified rosin, terpene resin, phenol resin, aliphatic or alicyclic hydrocarbon resin such as low molecular weight polyethylene or low molecular weight polypropylene, aromatic petroleum resin, chlorinated paraffin, paraffin wax, and others.

As the charge controller to be used in the toner of the present invention, positive or negative charge controllers known in the art can be used. Examples of charge controllers known nowadays in the technical field concerned may include those as set forth below.

(1) As the controller which controls the toner to be positively chargeable, the following substances may be included:

nigrosine, azine type dyes containing alkyl group having 2 to 16 carbon atoms (e.g., C.I. Basic Yellow 2 (C.I. 41000), C.I. Basic Yellow 3, C.I. Basic Red 1 (C.I. 45160), C.I. Basic Red 9 (C.I. 42500), C.I. Basic Violet 1 (C.I. 42535), C.I. Basic Violet 3 (C.I. 42555), C.I. Basic Violet 10 (C.I. 45170), C.I. Basic Violet 14 (C.I. 42510), C.I. Basic Blue 1 (C.I. 42025), C.I. Basic Blue 3 (C.I. 51005), C.I. Basic Blue 5 (C.I. 42140), C.I. Basic Blue 7 (C.I. 42595), C.I. Basic Blue 9 (C.I. 52015), C.I. Basic Blue 24 (C.I. 52030), C.I. Basic Blue 25 (C.I. 52025), C.I. Basic Blue 26 (C.I. 44025), C.I. Basic Green 1 (C.I. 42040), C.I. Basic Green 4 (C.I. 42000) lake pigments of these basic dyes (lake-forming agent may be phosphotungstic acid, phosphomolybdic acid, phosphotungustomolybdic acid, tannic acid, lauric acid, gallic acid, ferricyanide, ferrocyanide), C.I. Solvent Black 3 (C.I. 26150), Hansa Yellow G (C.I. 11680), C.I. Mordant Black 11, C.I. Pigment Black 1.

For example, there may be employed benzoylmethyl-hexadecylammonium chloride, decyl-trimethylammonium chloride or dialkyltin compounds such as dibutyltin or dioctyltin, metal salts of higher fatty acids, inorganic fine powder such as that of zinc oxice and metal complexes of EDTA, acetylacetone, vinyl type polymers containing amino group, polyamine resin of condensed type polymer containing amino group. Particularly, in view of dispersibility, nigrosine, metal salts of higher fatty acids and vinyl type polymers having amino group are preferred.

(2) As the controller which controls the toner to be negatively chargeable, there are the following substances. First of all, those as described in Japanese Patent Publications JP-B 41-20153, 42-27596, 44-6397, 45-26478 may be included.

There are also dyes or pigments such as nitrohumic acid and salts thereof or C.I. 14645 as disclosed in Japanese Laid-Open Patent Application JP-A 50-133338; Zn, Al, Co, Cr, Fe metal complexes of salicylic acid, naphthoic acid, dicarboxylic acid; sulfonated copper phthalocyanine pigment; styrene oligomers having nitrile group or halogen introduced therein, and chlorinated paraffins. Particularly, from the aspect of dispersibility, metal complexes of monoazo dyes, metal complexes of salicyclic acid, alkylsalicylic acid, naphthoic acid, diacrboxylic acid are preferred.

The toner of the present invention can be also mixed with other additives, if desired, to give good results. Examples of such additives may include lubricants such as Teflon, zinc stearate, polyvinylidene fluoride (among them, polyvinylidene fluoride is preferred); abrasives such as cerium oxide, silicon carbide, strontium titanate (among them, strontium titanate is preferred); flowability-imparting agents such as colloidal silica, aluminum oxide (among them, hydrophobic colloidal silica is particularly preferred); caking preventives; conductivity-imparting agents such as carbon black, zinc oxide, antimony oxide, tin oxide; fixing aids such as low-molecular weight polyethylene, low-molecular weight polypropylene, various waxes; or anti-offset agents. It is also possible to use a small amount of white fine particles and black fine particles of the opposite polarity as the developability improving agent.

Further, when the toner of the present invention is used as a two-component system developer, it is used in the form of a mixture with carrier powder. In this case, the mixing ratio of the toner and the carrier powder may be 0.1 to 50 wt.% in terms of the toner concentration, preferably 0.5 to 10 wt.%, more preferably 3 to 5 wt.%.

As the carrier which can be used in the present invention, those known in the art may be available. For example, powder having magnetic property such as iron powder, ferrite powder, nickel powder, glass beads, etc., and these materials subjected to the surface treatment with fluorine type resin or silicon type resin, may be employed.

Further, the toner of the present invention can be used also as a magnetic toner by further incorporating a magnetic material. In this case, the magnetic material also functions as a colorant. The magnetic material to be contained in the magnetic toner of the present invention may include iron oxides such as magnetite, hematite, ferrite or compounds of divalent metal and iron oxide; metal such as iron, cobalt, nickel or alloys of these metals with metals such as aluminum, cobalt, copper, lead, magnesium, tin, zinc, antimony, beryllium, bismuth, cadmium, calcium, manganese, selenium, titanium, tungsten, vanadium, and mixtures thereof.

These ferromagnetic materials may have average particle size of 0.1 to 2 μm, preferably about 0.1 to 0.5 μm, particularly preferably with spherical shapes. The amount contained in the toner may be about 20 to 200 parts by weight based on 100 parts by weight of the resin component, particularly preferably 40 to 180 parts by weight based on 100 parts by weight of the resin component.

Further, in the toner of the present invention, a colorant may be added, as desired.

As the colorant to be used in the toner of the present invention, any desired appropriate pigment or dye may be employed. For example, the pigment may include carbon black, aniline black, acetylene black, naphthol yellow, hansa yellow, rhodamine lake, alizarine lake, blood red, phthalocyanine blue, indanthrene blue. These may be used in amounts necessary and sufficient to maintain the optical density of the fixed image, namely 0.1 to 20 parts by weight, preferably 2 to 10 parts by weight, per 100 parts by weight of the resin. For similar purpose, dyes may be employed. For example, there are azo type dyes, anthraquinone type dyes, xanthene type dyes, methine dyes, which may be added in amounts of 0.1 to 20 parts by weight, preferably 0.3 to 3 parts by weight, per 100 parts by weight of the resin.

For preparation of the toner for development of electrostatic images according to the present invention, the above resin composition according to the present invention and the charge controller, optionally a magnetic material, a pigment or dye as the colorant and additives are sufficiently blended by a mixer such as ball mill, and melted and kneaded by a hot kneader such as heated rollers, kneader, extruder to have the pigment or dye dispersed or dissolved in the resins which have been made compatible with each other, and after solidification by cooling, pulverized and classified, whereby a toner with an average particle size of 3 to 20 μm can be obtained.

The present invention is described in detail below by referring to Examples, by which the present invention is not limited at all. In the following formulations, parts are parts by weight.

Synthesis Example 1

Into a reactor, 200 parts by weight of cumene were charged and the temperature was raised to the reflux temperature. To this was added dropwise a mixture of 100 parts by weight of styrene monomer and 9 parts of di-tert-butyl peroxide under cumene reflux over 4 hours. Further, under cumene reflux, solution polymerization was completed (146°C - 156°C), and cumene was removed. The polystyrene obtained was found to be soluble in IHF, with Mw = 3,700, Mw/Mn = 2.64, and the main peak of GPC was positioned at a molecular weight of 3,500, with Tg = 57°C. The GPC chromatogram of the polystyrene is shown in Figure 3.

The above polystyrene (30 parts by weight) was dissolved in the monomer mixture shown below to provide a mixed solution.

Monomer mixture	Formulated ratio
Styrene monomer	54 wt. parts
n-Butyl acrylate monomer	16 wt. parts
Divinylbenzene	0.3 wt. part
Benzoyl peroxide	1 wt. part
tert-Butylperoxy-2-ethyl-hexanoate	0.7 wt. part

Into the above mixed solution, 170 parts by weight of water containing 0.1 part by weight of a partially saponified polyvinyl alcohol dissolved therein were added to form a suspension. The above suspension was added into a reactor charged with 15 parts by weight of water and replaced with nitrogen, and suspension poly-

merization was carried out at a reaction temperature of 70 to 95°C for 6 hours. After completion of the reaction, the product was filtered off, dehydrated and dried to give a composition of a polystyrene and a styrene-n-butyl acrylate copolymer. This composition contained THF-insoluble and THF-soluble homogeneously mixed therein, and the polystyrene and the styrene-n-butyl acrylate copolymer were found to be homogeneously mixed. The content of the THF-insoluble (measured as the powder of 24 mesh pass, 60 mesh on) was 40 wt.%. More specifically, the THF-insoluble content was measured by placing about 0.5 g of the resin composition in a cylindrical filter paper (28×100 mm, No. 86R, produced by Toyo Roshi K.K.) and effecting the extraction with a Soxhlet's extractor at an average rate of about 7 times/hr. The molecular weight distribution of the THF-soluble was measured to give a result that there were peaks at the positions of about 0.4×10^4 and about 3.4×10^4 in the GPC chart, with Mn = 0.56×10^4, Mw = 13×10^4, Mw/Mn = 23, and the molecular weights of 10^4 or lower being 21 wt.%. Further, Tg of the resin was 59°C, and the glass transition point Tg_1 of the components of 10^4 or less separated by GPC was 57°C.

Figure 2 shows the GPC chromatogram of the THF-soluble.

The characteristics concerning molecular weights of the respective resins and resin compositions were measured according to the following method.

By use of Shodex KF-80M as the column for GPC measurement, it was assembled in the heat chamber of 40°C of a GPC measuring device (150C ALC/GPC produced by Waters Co.), and GPC operation was effected by injecting 200 µl of a sample (about 0.1 wt.% concentration of THF-soluble) under the condition of THF flow rate of 1 ml/min. and by using an RI for the detector. As the calibration curve for molecular weight measurement, THF solutions of mono-dispersed polystyrene standard materials (produced by Waters Co.) of the 10 points of molecular weights of 0.5×10^3, 2.35×10^3, 10.2×10^3, 35×10^3, 110×10^3, 200×10^3, 470×10^3, 1200×10^3, 2700×10^3 and 8420×10^3 were used.

Comparative Synthesis Example 1

The polystyrene obtained in Synthesis Example 1 (30 parts by weight) was dissolved in the following monomer mixture to provide a mixed solution.

Monomer mixture	Formulated ratio
Styrene monomer	54 wt. parts
n-Butyl acrylate monomer	16 wt. parts
Divinylbenzene	1.5 wt. parts
Benzoyl peroxide	1 wt. part

The above mixture was subjected to suspension polymerization in the same manner as in Synthesis Example 1 to obtain a composition of a polystyrene and a styrene-n-butyl acrylate copolymer. The content of THF-insoluble in this resin was 75 wt. %, thus containing a large amount of THF-insoluble.

Comparative Synthesis Example 2

The polystyrene obtained in Synthesis Example 1 (30 parts by weight) was dissolved in the following monomer mixture to provide a mixed solution.

Monomer mixture	Formulated ratio
Styrene monomer	54 wt. parts
n-Butyl acrylate monomer	16 wt. parts
Divinylbenzene	0.13 wt. part
tert-Butylperoxyhexanoate	1.0 wt. part

The above mixture was subjected to suspension polymerization in the same manner as in Synthesis Example 1 to obtain a composition of a polystyrene and a styrene-n-butyl acrylate copolymer. In the GPC chromatogram of the THF-soluble of this composition, there were peaks at the positions of a molecular weight of about 4,000 and a molecular weight of 15×10^4.

Comparative Synthesis Example 3

Into a reactor, 150 parts by weight of xylene was charged and the temperature was raised to the reflux temperature. To this was added dropwise a mixture of 100 parts by weight of styrene monomer, 2 parts by weight of tert-butylperoxybenzoate, and 1 part by weight of di-tertbutylperoxide under xylene reflux in 4 hours. Further, solution polymerization was completed under xylene reflux (138 - 144°C), and xylene was removed.

The polystyrene obtained was soluble in THF, with Mw = 10,000, Mw/Mn = 3.22, and the main peak was positioned at a molecular weight of 11,000, with Tg = 82°C.

The above polystyrene (30 parts by weight) was dissolved in the monomer mixture shown below to provide a mixed solution.

Monomer mixture	Formulated ratio
Styrene monomer	52 wt. parts
n-Butyl acrylate monomer	18 "
Divinylbenzene	0.25 "
Benzoyl peroxide	0.4 "
tert-Butylperoxy-2-ethylhexanoate	1 "

The above mixture was subjected to suspension polymerization in the same manner as in Synthesis Example 1 to obtain a composition of a polystyrene and a styrene-n-butyl acrylate copolymer. In the GPC chromatogram of the THF-soluble of this composition, there was substantially no peak at molecular weights of about 10,000 or less.

Comparative Synthesis Example 4

In the monomer mixture shown below, 170 parts by weight of water containing 0.1 part by weight of a partially saponified polyvinyl alcohol dissolved therein were added to provide a suspension.

Monomer mixture	Formulated ratio
Styrene monomer	70 wt. parts
α-Methylstyrene monomer	6 "
n-Butyl acrylate monomer	23 "
Divinylbenzene	0.9 "
Benzoyl peroxide	3 "

The above suspension was added into a reactor charged with 15 parts by weight of water and replaced with nitrogen, and suspension polymerization was carried out at a reaction temperature of 70 - 95°C for 6 hours. After completion of the reaction, the product was filtered off, dehydrated and dried to give a styrene-n-butyl acrylate copolymer.

The copolymer had a main peak at a molecular weight of about 17,000, and substantially no peak at molecular weights of 10^4 or less.

Synthesis Example 2

Into a reactor, 150 parts by weight of cumene was charged, and the temperature was raised to the reflux temperature. The following mixture was added dropwise under cumene reflux over 4 hours.

Monomer mixture	Formulated ratio
Styrene monomer	97.5 wt. parts
n-Butyl acrylate monomer	2.5 "
Di-tert-butyl peroxide	4 "

Further, polymerization was completed under cumene reflux (146 - 156°C) and cumene was removed. The styrene-n-butyl acrylate copolymer obtained had Mw = 6,900, Mw/Mn = 2.3 a main peak at a molecular weight of 7,100, and Tg = 60°C.

The above styrene-n-butyl acrylate copolymer (40 parts by weight) was dissolved in the following monomer mixture to provide a mixture.

Monomer mixture	Formulated ratio
Styrene monomer	38 wt. parts
n-Butyl methacrylate monomer	22 "
Divinylbenzene	0.24 "
Benzoyl peroxide	0.65 "
tert-Butylperoxy-2-ethyl-hexanoate	0.85 "

Into the above mixture, 170 parts by weight of water containing 0.1 part by weight of a partially saponified polyvinyl alcohol dissolved therein were added to form a suspension.

The above suspension was added into a reactor charged with 15 parts by weight of water and replaced with nitrogen, and the reaction was carried out at a temperature of 70 to 95°C for 6 hours. After completion of the reaction, the product was filtered, dehydrated and dried to give a composition of a styrene-n-butyl acrylate copolymer and a styrene-n-butyl methacrylate copolymer.

Synthesis Example 3

Into a reactor, 200 parts by weight of cumene were charged, and the temperature was raised to the reflux temperature. The following mixture was added dropwise under cumene reflux over 4 hours.

Monomer mixture	Formulated ratio
Styrene monomer	100 wt. parts
Di-tert-butylperoxide	8 "

Further, polymerization was completed under cumene reflux (146 - 156°C) and cumene was removed. The polystyrene obtained had Mw = 3,700, Mw/Mn = 2.64, a main peak at a molecular weight of 3,500, and Tg = 57°C.

The above polystyrene (30 parts by weight) was dissolved in the following monomer mixture to provide a

mixture.

Monomer mixture	Formulated ratio
Styrene monomer	56 wt. parts
2-Ethylhexyl acrylate monomer	14 "
Divinylbenzene	0.14 "
tert-Butylperoxy-2-ethylhexanoate	1.6 wt. parts

Into the above mixture, 170 parts by weight of water containing 0.1 part by weight of a partially saponified polyvinyl alcohol dissolved therein were added to form a suspension.

The above suspension was added into a reactor charged with 15 parts by, weight of water and replaced with nitrogen, and the reaction was carried out at a temperature of 70 to 95°C for 6 hours. After completion of the reaction, the product was filtered, dehydrated and dried to give a composition of a polystyrene and a styrene-2-ethylhexyl acrylate copolymer.

Synthesis Example 4

Into a reactor, 150 parts by weight of cumene were charged, and the temperature was raised to the reflux temperature. The following mixture was added dropwise under cumene reflux over 4 hours.

Monomer mixture	Formulated ratio
Styrene monomer	100 wt. parts
Di-tert-butyl peroxide	4 wt. parts

Further, polymerization was completed under cumene reflux (146 - 156°C) and cumene was removed. The polystyrene obtained had Mw = 5,200, Mw/Mn = 2.74, a main peak at a molecular weight of 5,300 and Tg = 75°C.

The above polystyrene (50 parts by weight) was dissolved in the following monomer mixture to provide a mixture.

Monomer mixture	Formulated ratio
Styrene monomer	37 wt. parts
n-Butyl acrylate monomer	13 "
Divinylbenzene	0.2 "
Benzoyl peroxide	0.8 "

Into the above mixture, 170 parts by weight of water containing 0.1 part by weight of a partially saponified polyvinyl alcohol dissolved therein were added to form a suspension.

The above suspension was added into a reactor charged with 15 parts by weight of water and replaced with nitrogen, and the reaction was carried out at a temperature of 70 to 95°C for 6 hours. After completion of the reaction, the product was filtered, dehydrated and dried to give a composition of a polystyrene and a styrene-n-butyl acrylate copolymer.

Synthesis Example 5

Into a reactor, 200 parts by weight of cumene were charged, and the temperature was raised to the reflux temperature. The following mixture was added dropwise under cumene reflux over 4 hours.

Monomer mixture	Formulated ratio
Styrene monomer	90 wt. parts
Methyl methacrylate monomer	10 "
Di-tert-butyl peroxide	8 "

Further, polymerization was completed under cumene reflux (146 - 156°C) and cumene was removed. The styrene-methyl methacrylate copolymer obtained had Mw = 3,900, Mw/Mn = 2.6, a main peak at a molecular weight of 4,100, and Tg = 60°C.

The above styrene-methyl methacrylate copolymer (30 parts by weight) was dissolved in the following monomer mixture to provide a mixture.

Monomer mixture	Formulated ratio
Styrene monomer	54 wt. parts
n-Butyl methacrylate monomer	16 "
Divinylbenzene	0.3 "
Benzoyl peroxide	1.4 "

Into the above mixture, 170 parts by weight of water containing 0.1 part by weight of a partially saponified polyvinyl alcohol dissolved therein were added to form a suspension. The above suspension was added into a reactor charged with 15 parts by weight of water and replaced with nitrogen, and the reaction was carried out at a temperature of 70 to 95°C for 6 hours. After completion of the reaction, the product was filtered, dehydrated and dried to give a composition of a styrene-methyl methacrylate copolymer and a styrene-n-butyl methacrylate copolymer.

Synthesis Example 6

Into a reactor, 200 parts by weight of cumene was charged, and the temperature was raised to the reflux temperature. The following mixture was added dropwise under cumene reflux over 4 hours.

Monomer mixture	Formulated ratio
Styrene monomer	95 wt. parts
α-Methylstyrene	5 wt. parts
Di-tert-butyl peroxide	8 wt. parts

Further, polymerization was completed under cumene reflux (146 - 156°C) and cumene was removed. The styrene-α-methylstyrene copolymer obtained had Mw = 4,500, Mw/Mn = 2.8, a main peak at a molecular weight of 4,400 and Tg = 63°C

The above styrene-methyl methacrylate copolymer (30 parts by weight) was dissolved in the following monomer mixture to provide a mixture.

Monomer mixture	Formulated ratio
Styrene monomer	53 wt. parts
n-Butyl methacrylate monomer	17 wt. parts
Divinylbenzene	0.3 wt. part
Benzoyl peroxide	1.4 wt. parts

Into the above mixture, 170 parts by weight of water containing 0.1 part by weight of a partially saponified polyvinyl alcohol dissolved therein was added to form a suspension. The above suspension was added into a reactor charged with 15 parts by weight of water and replaced with nitrogen, and the reaction was carried out at a temperature of 70 to 95°C for 6 hours. After completion of the reaction, the product was filtered, dehydrated and dried to give a composition of a styrene-α-methylstyrene copolymer and a styrene-n-butyl methacrylate copolymer.

Comparative Synthesis Example 5

Into a reactor, 200 parts by weight of cumene were charged, and the temperature was raised to the reflux temperature. The following mixture was added dropwise under cumene reflux over 4 hours.

Monomer mixture	Formulated ratio
Styrene monomer	100 wt. parts
Di-tert-butyl peroxide	8 "

Further, polymerization was completed under cumene reflux (146 - 156°C) and cumene was removed. The polystyrene obtained had Mw = 3,700, Mw/Mn = 2.64, a main peak at a molecular weight of 3,500, and Tg = 57°C.

The above polystyrene (30 parts by weight) was dissolved in the following monomer mixture to provide a mixture.

Monomer mixture	Formulated ratio
Styrene monomer	56 wt. parts
n-Butyl acrylate monomer	14 wt. parts
Divinylbenzene	0.05 wt. part
Benzoyl peroxide	2 wt. parts

Into the above mixture, 170 parts by weight of water containing 0.1 part by weight of a partially saponified polyvinyl alcohol dissolved therein was added to form a suspension.

The above suspension was added into a reactor charged with 15 parts by weight of water and replaced with nitrogen, and the reaction was carried out at a temperature of 70 to 95°C for 6 hours. After completion of the reaction, the product was filtered, dehydrated and dried to give a composition of a polystyrene and a styrene-n-butyl acrylate copolymer. This composition contained about 3 wt. % of THF-insoluble, thus containing only a small amount of THF-insoluble.

Example 1

Resin composition of Synthesis Example 1	100 wt. parts
Magnetic material	60 "
Negative charge controlling agent	2 "
Low-molecular weight polypropylene	3 "

The above materials were premixed by a Henschel mixer and then kneaded on a two-roll mill heated to 150°C for 20 minutes. After the kneaded product was left to cool, it was coarsely crushed by a cutter mill, then pulverized with the use of a micro-pulverizer by use of jet air stream, further classified by a wind-force classifier to obtain black fine powder with a volume-average particle size of 11.5 μm. The GPC chart of the THF-soluble of the black fine powder is shown in Figure 1.

A developer (toner) was obtained by dry blending 0.4 part by weight of hydrophobic colloidal silica fine powder with 100 parts by weight of the black fine powder.

The pulverizability of a kneaded cooled product for toner can be represented by a treating rate, i.e., the amount of the product which can be pulverized per unit time and, in the case of this toner, the rate was very good as 15 kg/hr under an air pressure of 5.5 kg/cm^2. No sticking occurred within the pulverizer.

Anti-blocking characteristic was examined by placing about 10 g of the toner in a plastic cup of 100 cc, and the change in agglomeration degree when the toner was left to stand at 50°C for. one day was examined. The agglomeration degree was measured by a powder tester produced by Hosokawa Micron K.K. The product left to stand at room temperature and the product left to stand at 50°C for one day exhibited substantially the same values of 10 wt. % and 12. wt.%, respectively, with the difference (ΔG) being 2 %. From this result, it was confirmed that substantially no blocking occurred.

Fixability, anti-offset characteristic, anti-winding characteristic and image quality, successive copying characteristics were examined by means of a high speed copying machine (NP-8570 produced by Canon K.K., 70 sheets per minute, 100 V).

Particularly, anti-offset characteristic was evaluated by dismantling the cleaning mechanism of the fixing rollers and counting the number of the sheets of successive copying after which the image or the rollers were contaminated.

The test was conducted by lowering the set temperature of the fixer by 5°C. Fixability was measured by rubbing the image with Silbon C paper reciprocally for 10 times under a load of about 100 g, and peeling of the image was represented by a lowering in percentage (%) of the reflective density. The evaluation of image was effected on a 200th sheet when 200 copies were continuously taken.

Anti-winding characteristic was evaluated by copying three sheets of a whole surface black image and by observing the trace remaining on the copies of a pawl for peeling attached to the fixing roller to judge how the peeling relied on the pawl.

As the result, fixability was very good with a lowering in percentage of 3 %, anti-offset characteristic was good without any contamination on image or roller, and anti-winding characteristic was very good, although a trace of the pawl showing the reliance on the pawl was slightly observed on the image.

By using an image with an image area ratio of about 5 %, a successive copying test of 50,000 sheets was conducted, whereby good images were obtained without sticking or filming onto the photosensitive member.

Comparative Examples 1 - 5

By use of the resin compositions prepared in Comparative Synthesis Examples 1 - 5 in place of the resin composition in Example 1, toners were prepared in the same manner as in Example 1, and the toners thus obtained were called Comparative Examples 1 - 5.

The toners of Comparative Examples were evaluated to provide the results shown in Table 1.

Table 1

	Pulverizability (kg/hr)	Anti-sticking char.	Anti-blocking char. ΔG (%)	Fixability (%)	Anti-offset char. (sheets)	Anti-winding char.	Image quality	Successive copying char. (sheets)
Example 1	o (15)	o	o (2)	o (2)	o	o	o	o
Comparative Example 1	o (18)	×	× (40)	o (4)	× (700)	o	Δ**	× (5000)
" 2	× (5)	o	o (4)	× (15)	o	o	o	o
" 3	× (7)	o	o (5)	× (12)	o	o	o	o
" 4	o (15)	o	o (4)	× (13)	× (1000)	×	o	o
" 5	× (8)	o	o (6)	o (6)	× (500)	×	o	o

**: Low density

Example 2

Resin composition of Synthesis Example 2	100 wt. parts
Magnetic material	60 wt. parts
Positive charge controlling agent	2 wt. parts
Low molecular weight polypropylene	4 wt. parts

Black fine powder was prepared from the above mixture and then a toner was prepared in the same manner as in Example 1. The black fine powder had a volume average particle size of 11.7 μm.

A colloidal silica fine powder treated with an amino-modified silicone oil was employed.

The pulverizability of the kneaded cooled product for toner was very good as indicated by the treating rate of 16 kg/hr. No sticking occurred in the pulverizer. There was no problem in anti-blocking characteristic with $\Delta G = 3$ %.

Image quality and fixing relationship were evaluated by a personal copying machine (FC-5 produced by Canon K.K.).

As the result, image quality was good, with good images being continually produced until there was no toner, and there was neither filming nor sticking onto the photosensitive member.

With the set temperature in the fixer being lowered by 10°C, the cleaning mechanism in the fixer was removed and the above image formation was effected to give the result that fixability was very good with a lowing in percentage-reflective density of about 0 %, without problems in anti-offset characteristic or anti-winding characteristic.

Example 3

Except for changing the resin composition in Example 2 to the resin composition of Synthesis Example 3, black fine powder was prepared, and then a toner was prepared in the same manner as in Example 2.

The black powder had a volume-average particle size of 11.3 μm.

The pulverizability of the kneaded cooled product for toner was very good as the treating rate of 15.5 kg/hr. Also, no sticking occurred in the pulverizer.

There was no problem at all in anti-blocking characteristic with $\Delta G = 2$ %.

Image quality and fixing relationship were evaluated by a copying machine (NP-5540 produced by Canon K.K.; OPC photosensitive member, 40 sheets per minute).

As the result, good images were stably obtained by successive copying of 50,000 sheets. There was no filming or sticking onto the photo-sensitive member.

With the set temperature in the fixer being lowered by 10°C, the cleaning mechanism in the fixer was removed and the above successive copying was conducted to give a result that fixability was very good with a lowering in percentage-reflective density of about 3 %, without problems in anti-offset characteristic and anti-winding characteristic.

Example 4

Except for changing the resin composition in Example 2 to the resin composition of Synthesis Example 4, black fine powder was prepared, and then a toner was prepared in the same manner as in Example 2.

The black powder had a volume-average particle size of 11.7 μm.

The pulverizability of the kneaded cooled product for toner was very good as the treating rate of 15.2 kg/hr. No sticking occurred in the pulverizer. There was no problem at all in anti-blocking characteristic with $\Delta G = 3$%.

Image quality and fixing relationship were evaluated by a digital copying machine using an amorphous Si photosensitive member (NP-9030 produced by Canon K.K.). As the result, good images were stably obtained by successive copying of 50,000 sheets. There was no filming or sticking onto the photosensitive member.

With the set temperature in the fixer being lowered by 10°C, the cleaning mechanism in the fixer was removed and the above successive copying was conducted to give a result that fixability was very good with a

Except for changing the resin composition in Example 1 to the resin composition of Synthesis Example 5, black fine powder was prepared, and then a toner was prepared in the same manner as in Example 1.

The black powder had a volume-average particle size of 11.4 μm.

The pulverizability of the kneaded cooled product for toner was very good as the treating rate of 17.1 kg/hr. No sticking occurred in the pulverizer. There was no problem at all in anti-blocking characteristic with $\Delta G = 3$ %.

Image quality and fixing relationship were evaluated by a copying machine (NP-400 RE produced by Canon K.K.).

As the result, good images were stably obtained by successive copying of 50,000 sheets. There was no filming or sticking onto the photosensitive member.

With the set temperature in the fixer being lowered by 10°C, the cleaning mechanism in the fixer was removed and the above successive copying was conducted to give a result that fixability was very good with a lowering in percentage-reflective density of about 4 %, without problems in anti-offset characteristic or anti-winding characteristic.

Example 6

Resin composition of Synthesis Example 6	100 wt. parts
Carbon black	6 wt. parts
Positive charge controlling agent	2 wt. parts
Low-molecular weight polypropylene	3 wt. parts

Black fine powder was prepared from the above mixture and then a toner was prepared in the same manner as in Example 1. This toner was mixed with about 10 wt. % of iron powder with particle sizes of 200 - 300 mesh to provide a developer.

The pulverizability of the kneaded cooled product for toner was very good as the treating rate of 15.2 kg/hr. No sticking occurred in the pulverizer. There was no problem in anti-blocking characteristic with $\Delta G = 4$ %.

Image quality and fixing relationship were evaluated by an ultra-high speed copying machine (NP-8500 Super produced by Canon K.K.). As the result, good quality of images could be stably obtained by successive copying of 100,000 sheets. There was neither filming nor sticking onto the drum.

With the set temperature in the fixer being lowered by 10°C, the cleaning mechanism in the fixer was removed and the above image formation was effected to give a result that fixability was very good with a lowering in percentage-reflective density of about 5 %, without problems in anti-offset characteristic or anti-winding characteristic.

The characteristic parameters of the above-described toners are inclusively shown in Table 2.

In the following, the present invention is described by referring to other Synthesis Examples and Examples. Parts in the following formulations are all parts by weight.

Synthesis Example 7

Into 200 parts of toluene at the boiling point, a mixture of 70 parts of styrene, 20 parts of n-butyl acrylate, 10 parts of α-methylstyrene and 6 parts of benzoyl peroxide was added dropwise over 5 hours, and thereafter polymerization was further carried out by maintaining the mixture at the boiling point for 3 hours, followed by removal by vacuum drying, to give a low-molecular weight polymer-1. Next, a homogeneous mixture of 70 g of the low-molecular weight polymer-1, 75 parts of styrene, 24 parts of n-butyl acrylate, 1 part of divinylbenzene and 4 parts of benzoyl peroxide, was suspended in 300 parts of water containing 0.8 part of a partially saponified polyvinyl alcohol dissolved therein, and polymerization was carried out at a temperature of 80°C for 15 hours to obtain a pearl-like resin composition in which from high-molecular weight polymers to low-molecular weight polymers were homogeneously mixed. The resin composition was dried under a reduced pressure to give a resin composition-7.

The resin composition-7 was accurately weighed in about 0.5 g, placed in a cylindrical filter paper (No. 86R produced by Toyo Roshi K.K.) and subjected to Soxlet's extraction by using 180 ml of chloroform for 6 hours. After evaporation for removal of the medium from the soluble extracted, the residue was vacuum-dried at 100°C for 12 hours, and the soluble resin component was weighed. From the original sample weight and this value, the gel component weight (crosslinking degree) was determined according to the formula as described before. Further, the soluble resin component was dissolved in THF to form a sample with 0.1 wt. % concentration and passed through a sample pretreatment filter for non-aqueous system to provide a sample for GPC. Shodex KF-80M as the column for GPC measurement was assembled in the heat chamber at 40°C of a GPC measuring device (150 C ALC/GPC produced by Waters Co.), and GPC was effected by injecting 200 µl of a sample (about 0.1 wt. % concentration of the THF-soluble) under the condition of THF flow rate of 1 ml/min and by using an RI for the detector. As the calibration curve for molecular weight measurement, THF solutions of mono-dispersed polystyrene standard materials (produced by Waters Co.) of the 10 points of molecular weights of 0.5×10^3, 2.35×10^3, 10.2×10^3, 35×10^3, 110×10^3, 200×10^3, 470×10^3, 1200×10^3, 2700×10^3 and 8420×10^3 were used.

The gel content in the resin composition-7 was found to be 33 wt. %, and the molecular weight main peak value of the eluted component was 6000 and the sub-peak value was 51000. Figure 10 shows the chromatogram by GPC.

Synthesis Example 8

In the suspension polymerization, 120 parts of the low-molecular weight polymer, 0.5 parts of divinylbenzene and 2 parts of t-butylperoxy-2-ethylhexanoate as the polymerization initiator were used, and following otherwise the same procedure as in Synthesis Example 7, a pearl-like resin composition-8 was obtained. This resin composition showed a gel component of 5 wt.%, with the main peak value of molecular weight of the eluted component being 5000 and the shoulder value 82000.

Synthesis Example 9

In the suspension polymerization, 1.4 parts of divinylbenzene and 4.5 parts of benzyl peroxide as the polymerization initiator were used, and following otherwise the same procedure as in Synthesis Example 7, a pearl-like resin composition-9 was obtained. The resin composition contained a gel component of 45 wt. %, with the main peak value of molecular weight of the eluted component being 5000 and the shoulder value 31000.

Synthesis Example 10

In the suspension polymerization, 60 parts of the low molecular weight polymer, 1.9 parts of divinylbenzene and 4.5 parts of benzoyl peroxide as the polymerization initiator were used, and following otherwise the same procedure as in Synthesis Example 7, a pearl-like resin composition-10 was obtained. This resin composition contained a gel component of 55 wt. %, with the main peak value of molecular weight of the eluted component being 5000 and the shoulder value 33000.

Synthesis Example 11

In the suspension polymerization, 1 part of triethylene glycol diacrylate was used as the crosslinking agent in place of divinylbenzene, and following otherwise the same procedure as in Synthesis Example 7, a pearl-like resin composition-11 was obtained. This resin composition contained a gel component of 27 wt. %, with

the main peak value of molecular weight of the eluted component being 5800 and the sub-peak value 48000.

Comparative Synthesis Example 6

In synthesis of the low-molecular weight polymer, carbon tetrachloride was added to the solvent, and 65 parts of styrene, 15 parts of α-methylstyrene and 7 parts of benzoyl peroxide were used, and following otherwise the same procedure for synthesis of the low-molecular weight polymer-1 as in Synthesis Example 7, a low-molecular weight polymer-2 was obtained. Next, the same procedure as in Synthesis Example 7 was repeated except for using 70 parts of the low-molecular weight polymer-2, 8 parts of α-methylstyrene and 5 parts of benzoyl peroxide, to obtain a pearl-like comparative resin composition-6. This resin composition had a gel component of 30 wt. %, with the main peak value of the eluted component being 900, and the shoulder value 13000.

Comparative Synthesis Example 7

In synthesis of the low-molecular weight polymer, without use of α-methylstyrene and by use of correspondingly increased amount of styrene and 3 parts of benzoyl peroxide, and following otherwise the same procedure for synthesis of the low-molecular weight polymer-1 as in Synthesis Example 7, a low-molecular weight polymer-3 was obtained. Next, the same procedure as in Synthesis Example 7 was repeated except for using 70 parts of the low-molecular weight polymer-3, 0.8 part of t-butylperoxy-2-ethylhexanoate, to obtain a pearl-like comparative resin composition-7. This resin composition had a gel component of 36 wt.%, with the main peak value of the eluted component being 28000, and the sub-peak value 98000.

Comparative Synthesis Example 8

Synthesis Example 7 was repeated except for adding 15 parts of the low-molecular weight-1 in Synthesis Example 7, 2.2 parts of divinylbenzene and 2 parts of t-butylperoxy-2-ethylhexanoate as the initiator, to obtain a pearl-like comparative resin composition-8. This resin composition had a gel component of 76 wt. %, with the main peak value of the eluted component being 8000, and the sub-peak value 86000.

Comparative Synthesis Example 9

In synthesis of the low-molecular weight polymer, without use of α-methylstyrene and by use of correspondingly increased amount of styrene and 2.5 parts of benzoyl peroxide, and following otherwise the same procedure for synthesis of the low-molecular weight polymer-1 as in Synthesis Example 7, a low-molecular weight polymer-4 was obtained. Next, the same procedure as in Synthesis Example 7 was repeated except for using 70 parts of the low-molecular weight polymer-4 and 0.6 part of t-butylperoxy-2-ethylhexanoate, to obtain a pearl-like comparative resin composition-9. This resin composition had a gel component of 32 wt. %, with the main peak value of the eluted component being 113000, and the sub-peak value 27000. Figure 11 shows the GPC chart of the eluted component.

Comparative Synthesis Example 10

The procedure of Comparative Synthesis Example 7 was repeated except for using 70 parts of the low-molecular weight polymer-3 and 0.5 part of t-butylperoxy-2-ethylhexanoate, to obtain a pearl-like comparative resin composition-10. This resin composition had a gel component of 40 wt. %, with the main peak value of the eluted component being 23000, and the sub-peak value 195000.

Synthesis Example 12

A pearl-like resin composition-12 was obtained in the same manner as in Synthesis Example 7 except for using 20 parts of the low-molecular weight polymer-1 in Synthesis Example 7, 1.3 parts of divinylbenzene and 4.5 parts of benzoyl peroxide as the initiator in the suspension polymerization. This resin composition had a gel component of 45 wt. %, with the main peak value of the eluted component being 25000, and the shoulder value 5000.

Synthesis Example 13

A pearl-like resin composition-13 was obtained in the same manner as in Synthesis Example 7 except for using 1.3 parts of triethylene glycol diacrylate and 4.5 parts of benzoyl peroxide as the initiator in the suspension polymerization. This resin composition had a gel component of 41 wt. %, with the main peak value of the eluted component being 5000, and the shoulder value 36000.

Synthesis Example 14

A low molecular weight polymer-5 was obtained in the same manner as in synthesis of the low molecular weight polymer-1 is Synthesis Example 7 except for using 15 parts of 2-ethylhexyl acrylate and 75 parts of styrene. Next, except for using 70 parts of the low molecular weight polymer-5, Synthesis Example 7 was repeated to obtain a pearl-like resin composition-14. This resin composition had a gel component of 29 wt. %, with the main peak value of the eluted component being 5500, and the sub-peak value 48000.

The proportions of the component A, the component B and the component C of the vinyl polymers obtained in the respective synthesis examples are shown in Table 3.

Table 3

	Component A	Component B	Component C
Synthesis Example 7	9 (%)	28 (%)	63 (%)
" 8	4	37	59
" 9	7	31	62
" 10	5	23	72
" 11	6	29	65
Comparative Synthesis Example 6	1	3	96
" 7	9	40	51
" 8	8	30	62
" 9	9	60	31
" 10	6	41	53
Synthesis Example 12	9	56	35
" 13	8	28	64
" 14	1	11	88

Example 7

Resin composition-7	100 parts
Magnetite	60 parts
Low-molecular weight polypropylene	4 parts
Nigrosine	2 parts

The above materials were blended well by a blender, and then kneaded on two rollers heated to 150°C. After the kneaded product was left to cool, crushed by a cutter mill, then pulverized by a micro-pulverizer by use of jet air stream, and further classified by means of a wind-force classifier to obtain black fine powder with a volume-average particle size of 11 to 12 μm. The black fine powder was mixed with 0.5 part by weight of silica produced by the wet process per 100 parts by weight thereof in a Henschel mixer to form a toner. The toner was subjected to successive copying of 3000 sheets by use of a copying machine (NP-3525 produced by Canon K.K.) in which an OPC photosensitive member was used. As the result, sharp images of high resolution with image density of 1.2 - 1.3 without fog were obtained. Further, by use of the fixer for the NP-3525 copying machine and by varying the fixing roller temperature, investigations were made about off-set, fixability, and winding. As the result, as shown in Table 4, no offset was generated from 140°C up to 230°C, and fixability at 150°C was also good without generation of winding around rollers. The kneaded product for toner was found to be excellent also in pulverizability and anti-blocking characteristic by the test at a temperature of 50°C for one day.

Example 8

A toner was prepared in the same manner as in Example 7 except for using 100 parts of the resin composition-8, and successive copying of 3000 sheets was conducted by use of a copying machine (NP-3525 produced by Canon K.K.), to give sharp images of high resolution with image density of 1.2 - 1.3 without fog. Further, by use of the NP-3525 fixer and by varying the fixing roller temperature, investigations were made about off-set, fixability, and winding. As the result, as shown in Table 4, no offset was generated from 140°C up to 230°C, and fixability at 150°C was also good without generation of winding around rollers. The kneaded product for toner was found to be good also in pulverizability and anti-blocking characteristic by the test at a temperature of 50°C for one day.

Example 9

A toner was prepared in the same manner as in Example 7 except for using 100 parts of the resin composition-9, and successive copying of 3000 sheets was conducted by use of a copying machine (NP-3525 produced by Canon K.K.), to give sharp images of high resolution with image density of 1.25 - 1.35 without fog. With the use of NP-3525 fixer, by varying the fixing roller temperature, investigations were made about off-set and fixability, winding. As the result, as shown in Table 4, no offset was generated from 140°C up to 230°C, and fixability at 150°C was also good without generation of winding around rollers. Further, there was no problem in anti-blocking characteristic by the test at a temperature of 50°C for one day, and also the kneaded product for toner was found to be excellent in pulverizability.

Example 10

After 100 parts of the resin composition-10, 60 parts of magnetite, 4 parts of a low molecular weight polypropylene and 2 parts of a salicylic chromium type complex compound were blended well by a blender, the blend was kneaded on two rollers heated to 150°C. After the kneaded product was left to cool, crushed by a cutter mill, then pulverized by a micropulverizer by use of jet air stream, and further classified by means of a wind-force classifier to obtain black fine powder with a volume-average particle size of 11 to 12 μm. The black fine powder was mixed with 0.4 part by weight of dry process silica subjected to hydrophobicity modification per 100 parts by weight of the black fine powder in a Henschel mixer to form a toner. The toner was subjected to successive copying of 3000 sheets by use of a copying machine (NP-7550 produced by Canon K.K.) in which an amorphous silicon photosensitive member was used. As the result, sharp images of high resolution with

image density of 1.2 - 1.3 without fog were obtained. Further, by use of the fixer for the NP-7550 copying machine and by varying the fixing roller temperature, investigations were made about off-set, fixability and winding. As the result, as shown in Table 4, no offset was generated from 140°C up to 230°C, and fixability at 150°C was also good without generation of winding around rollers. There was no problem in anti-blocking characteristic under the conditions of a temperature of 50°C for one day, and also the kneaded product for toner was found to be excellent in pulverizability.

Example 11

A toner was prepared in the same manner as in Example 7 except for using 100 parts of the resin composition-11, and successive copying of 3000 sheets was conducted by use of the NP-3525 copying machine to give sharp images of high resolution with image density of 1.15 - 1.3 without fog. With the use of the NP-3525 fixer, by varying the fixing roller temperature, investigations were made about off-set, fixability and winding. As the result, as shown in Table 4, no offset was generated from 140°C up to 230°C, and fixability at 150°C was also good without generation of winding around rollers. Further, there was no problem in anti-blocking characteristic under the conditions of a temperature of 50°C for one day, and also the kneaded product for toner was found to be excellent in pulverizability.

Example 12

A toner was prepared in the same manner as in Example 7 except for using 100 parts of the resin composition-12, and successive copying of 3000 sheets was conducted by use of the NP-3525 copying machine to give sharp images of high resolution with image density of 1.2 - 1.3 without fog. With the use of the NP-3525 fixer, by varying the fixing roller temperature, investigations were made about off-set, fixability and winding. As the result, as shown in Table 4, no offset was generated from 140°C up to 230°C, and fixability at 150°C was also good without generation of winding around rollers. Further, there was no problem in anti-blocking characteristic under the conditions of a temperature of 50°C for one day, and also the kneaded product for toner was found to be satisfactory in pulverizability.

Example 13

A toner was prepared in the same manner as in Example 7 except for using 100 parts of the resin composition-13, and successive copying of 3000 sheets was conducted by use of the NP-3525 copying machine to give sharp images of high resolution with image density of 1.15 - 1.3 without fog. With the use of the NP-3525 fixer, by varying the fixing roller temperature, investigations were made about off-set, fixability and winding. As the result, as shown in Table 4, no offset was generated from 140°C up to 230°C, and fixability at 150°C was also good without generation of winding around rollers. Further, there was no problem in anti-blocking characteristic under the conditions of a temperature of 50°C for one day, and also the kneaded product for toner was found to be excellent in pulverizability.

Example 14

A toner was prepared in the same manner as in Example 7 except for using 100 parts of the resin composition-14, and successive copying of 3000 sheets was conducted by use of the NP-3525 copying machine to give sharp images of high resolution with image density of 1.15 - 1.25 without fog. With the use of NP-3525 fixer, by varying the fixing roller temperature, investigations were made about off-set, fixability and winding. As the result, as shown in Table 4, no offset was generated from 140°C up to 230°C, and fixability at 150°C was also good without generation of winding around rollers. Further, there was no problem in anti-blocking characteristic under the conditions of a temperature of 50°C for one day, and also the kneaded product for toner was found to be excellent in pulverizability.

Comparative Example 6

A toner was prepared in the same manner as in Example 7 except for using 100 parts of the comparative resin composition-7, and successive copying of 3000 sheets was conducted by use of the NP-3525 copying machine, to give sharp images of high resolution with image density of 1.2 - 1.3 without fog. However, as shown in Table 5, in evaluation of anti-offset characteristic, fixability and winding by use of the NP-3525 fixer, fixability at 150°C had no problem, but offset at 140°C and offset at 230°C were noticeable, with winding around rollers

being generated. Further, under the conditions of 50°C and one day, blocking of toner was confirmed.

Comparative Example 7

A toner was prepared in the same manner as in Example 7 except for using 100 parts of the comparative resin composition-7, and successive copying of 3000 sheets was conducted by use of the NP-3525 copying machine, to give sharp images of high resolution with image density of 1.1 - 1.2 without fog. In evaluation of anti-offset characteristic, fixability and winding by the NP-3525 fixer, although no offset or winding at 230°C, blocking at 50°C for one day was generated, it was found that offset was generated at 140°C as shown in Table 5, the fixability at 150°C was poor, and the pulverizability of the kneaded product for toner was found to be remarkably inferior.

Comparative Example 8

A toner was prepared in the same manner as in Example 7 except for using 100 parts of the comparative resin composition-8, and successive copying of 3000 sheets was conducted by use of the NP-3525 copying machine, whereby only images with a shade of fog and with low image density of 0.95 - 1.15 could be obtained. In evaluation of offset, fixability, winding by the NP-3525 fixer, there was no problem in offset, winding at 230°C or anti-blocking characteristic at 50°C for one day, but fixability at 150°C and offset at 140°C were poor, and further the pulverizability of the kneaded product for toner was not satisfactory.

Comparative Example 9

A toner was prepared in the same manner as in Example 7 except for using 100 parts of the comparative resin composition-9, and successive copying of 3000 sheets was conducted by use of the NP-3525 copying machine whereby only images with a shade of fog and with low image density of 1.1 - 1.2 could be obtained. In evaluation of offset, fixability and winding by the NP-3525 fixer, no offset at 230°C, further no blocking or winding around rollers under the conditions of 50°C and one day was generated, but both offset at 140°C and fixability at 150°C were poor, and further the pulverizability of the kneaded product for toner was remarkably bad.

Comparative Example 10

A toner was prepared in the same manner as in Example 7 except for using 100 parts of the comparative resin composition-10, and successive copying of 3000 sheets was conducted by use of the NP-3525 copying machine, whereby images obtained had no fog but low image density of 1.05 - 1.15. In evaluation of offset, fixability and winding by the NP-3525 fixer, no offset at 230°C, no blocking or winding around rollers under the conditions of 50°C and one day was generated, but both offset at 140°C and fixability at 150°C were poor, and further the pulverizability of the kneaded product for toner was remarkably bad.

The results are summarized in the following Tables 4 and 5.

Table 4

Example	Anti-offset characteristic		Fixability	Anti-winding character-istic	Anti-blocking char.	Pulverizability
	140°C	230°C	150°C		50°C one day	
7	◎	◎	◎	○	○	○
8	○	○	◎	○	○	○
9	◎	◎	◎	○	○	○
10	○	◎	○	○	○	○
11	◎	◎	◎	○	○	○
12	○	○	Δ	○	○	Δ
13	◎	◎	◎	○	○	○
14	◎	◎	◎	○	○	○

Table 5

Comparative Example	Anti-offset characteristic		Fisability	Anti-winding characteristic	Anti-blocking char.	Pulverizability
	140°C	230°C	150°C		50°C one day	
6	×	×	o	×	×	o
7	×	◎	×	o	o	×
8	×	o	Δ	o	o	Δ
9	×	◎	×	o	o	×
10	×	×	×	o	o	×

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Example 15

Into a reactor, 200 parts by weight of cumene was charged and the temperature was raised to the reflux temperature. To the system was added dropwise a mixture of 100 parts by weight of styrene monomer and 8 parts of di-tert-butyl peroxide under cumene reflux over 4 hours. Further, under cumene reflux (146°C - 156°C), solution polymerization was completed, and cumene was removed. The polystyrene obtained was found to be soluble in THF, with Mw = 3700, Mw/Mn = 2.64, and the main peak of GPC was positioned at a molecular weight of 3500, with Tg = 57°C.

The above polystyrene (30 parts by weight) was dissolved in the monomer mixture shown below to provide a mixed solution.

Monomer mixture	Formulrated ratio
Styrene monomer	54 wt. parts
n-Butyl acrylate monomer	16 "
Divinylbenzene	0.3 "
Benzoyl peroxide	1.4 "

Into the above mixed solution, 170 parts by weight of water containing 0.1 part by weight of a partially saponified polyvinyl alcohol dissolved therein was added to form a suspension. The above suspension was added into a reactor charged with 15 parts by weight of water and replaced with nitrogen, and suspension polymerization was carried out at a reaction temperature of 70 to 95°C for 6 hours. After completion of the reaction, the product was filtered off, dehydrated and dried to give a composition of a polystyrene and a styrene-n-butyl acrylate copolymer. This composition contained THF-insoluble and THF-soluble homogeneously mixed therein, and the polystyrene and the styrene-n-butyl acrylate copolymer were found to be homogeneously mixed. The content of the THF-insoluble (measured as the powder of 24 mesh pass, 60 mesh on) was 25 wt.%. The molecular weight distribution of THF soluble was measured to give the result that there were peaks at the positions of about 0.4×10^4 and about 3.4×10^4 in the GPC chart, with Mn = 0.55×10^4, Mw = 13×10^4, Mw/Mn = 24, and the molecular weights of 10^4 or lower being 25 wt.%. Further, Tg of the resin was 58°C, and the glass transition point Tg_1 of the components of 10^4 or less separated by GPC was 57°C.

Figure 12 shows the GPC chromatogram of the THF-soluble. The chromatogram in Figure 12 was very approximate to the chromatogram in Figure 1.

The characteristics concerning molecular weights of the respective resins and resin compositions were measured according to the following method.

By use of shodex KF-80M as the column for GPC measurement, it was assembled in the heat chamber of 40°C of a GPC measuring device (150C ALC/GPC produced by Waters Co.), and GPC operation was effected by injecting 200 µl of a sample (about 0.1 wt.% concentration of THF-soluble) under the condition of THF flow rate of 1 ml/min and by using an RI for the detector. As the calibration curve for molecular weight measurement, THF solutions of mono-dispersed polystyrene standard materials (produced by Waters Co.) of the 10 points of molecular weights of 0.5×10^3, 2.35×10^3, 10.2×10^3, 35×10^3, 110×10^3, 200×10^3, 470×10^3, 1200×10^3, 2700×10^3 and 8420×10^3 were used.

Example 16

Into a reactor, 200 parts by weight of cumene was charged, and the temperature was raised to the reflux temperature. The following mixture was added dropwise under cumene reflux over 4 hours.

Monomer mixture	Formulated ratio
Styrene monomer	95 wt.parts
α-Methylstyrene monomer	5 "
Di-tert-butylperoxide	8 "

Further, polymerization was completed under cumene reflux (146 - 156°C) and the cumene was removed. The styrene-α-methylstyrene copolymer obtained had Mw = 4500, Mw/Mn = 2.8, a main peak at a molecular weight of 4400, and Tg = 63°C.

The above styrene-α-methylstyrene copolymer (30 parts by weight) was dissolved in the following monomer mixture to provide a mixed solution.

Monomer mixture	Formulated ratio
Styrene monomer	55 wt. parts
2-Ethylhexyl acrylate	15 "
Divinylbenzene	0.3 "
Benzoyl peroxide	1.4 "

Into the above mixture, 170 parts by weight of water containing 0.1 part by weight of a partially saponified polyvinyl alcohol dissolved therein was added to form a suspension.

The above suspension was added into a reactor charged with 15 parts by weight of water and replaced with nitrogen, and the reaction was carried out at a temperature of 70 to 95°C for 6 hours. After completion of the reaction, the product was filtered, dehydrated and dried to give a composition of a styrene-α-methylstyrene copolymer and a styrene-2-ethylhexyl acrylate copolymer.

The content of the THF-insoluble in this composition was 32 wt.%. The molecular weight distribution of THF-soluble was measured to give the result that there were peaks at the positions of 0.5×10^4 and 4.2×10^4, with Mn = 0.62×10^4, Mw = 13×10^4, Mw/Mn = 21, and the molecular weights of 10^4 or lower being 20 wt. %. Further, Tg of the resin was 58°C, and the glass transition point Tg_1 of the components of 10^4 or less separated by GPC was 60°C.

Example 17

Into a reactor, 200 parts by weight of cumene was charged, and the temperature was raised to the reflux temperature. The following mixture was added dropwise under cumene reflux over 4 hours.

Monomer mixture	Formulated ratio
Styrene monomer	90 wt. parts
Methyl methacrylate monomer	10 "
Di-tert-butyl peroxide	8 "

Further, polymerization was completed under cumene reflux (146 - 156°C) and cumene was removed. The styrene-methyl methacrylate copolymer obtained had Mw = 3900, Mw/Mn = 2.6, a main peak at a molecular weight of 4100, and Tg = 60°C.

The above styrene-methyl methacrylate copolymer (40 parts by weight) was dissolved in the following monomer mixture to provide a mixed solution.

Monomer mixture	Formulated ratio
Styrene monomer	38 wt. parts
n-Butyl methacrylate monomer	22 "
Divinylbenzene	0.24 "
Benzoyl peroxide	0.65 "
tert-Butylperoxy-2-ethylhexanoate	0.85 "

Into the above mixture, 170 parts by weight of water containing 0.1 part by weight of a partially saponified polyvinyl alcohol dissolved therein was added to form a suspension. The above suspension was added into a reactor charged with 15 parts by weight of water and replaced with nitrogen, and the reaction was carried out at a temperature of 70 to 95°C for 6 hours. After completion of the reaction, the product was filtered, dehydrated and dried to give a composition of a styrene-methyl methacrylate copolymer and a styrene-n-butyl methacrylate copolymer.

The content of the THF-insoluble in this composition was 35 wt. %. The molecular weight distribution of THF-soluble was measured to give the result that there were peaks at the positions of 0.4×10^4 and 4.3×10^4, with Mn = 0.59×10^4, Mw = 9.2×10^4, Mw/Mn = 16, and the molecular weights of 10^4 or lower being 32 wt. %. Further, Tg of the resin was 60°C, and the glass transition point Tg_1 of the components of 10^4 or less separated by GPC was 58°C.

Example 18

Into a reactor, 200 parts by weight of cumene was charged and the temperature was raised to the reflux temperature. The following mixture was added dropwise under cumene reflux over 4 hours.

Monomer mixture	Formulated ratio
Styrene monomer	100 wt. parts
Di-tert-butyl peroxide	8 "

Further, polymerization was completed under cumene reflux (146 - 156°C) and cumene was removed. The polystyrene obtained had Mw = 3700, Mw/Mn = 2.64, a main peak at a molecular weight of 3500, and Tg = 57°C.

The above polystyrene (30 parts by weight) was dissolved in the following monomer mixture to provide a mixed solution.

Monomer mixture	Formulated ratio
Styrene monomer	55 wt. parts
n-Butyl acrylate monomer	15 "
Divinylbenzene	0.14 "
tert-Butylperoxy-2-ethylhexanoate	1.6 "

Into the above mixture, 170 parts by weight of water containing 0.1 part by weight of a partially saponified polyvinyl alcohol dissolved therein was added to form a suspension. The above suspension was added into a reactor charged with 15 parts by weight of water and replaced with nitrogen, and the reaction was carried out at a temperature of 70 to 95°C for 6 hours. After completion of the reaction, the product was filtered, dehydrated

and dried to give a composition of a polystyrene and a styrene-n-butyl acrylate copolymer.

The content of the THF-insoluble in this composition was 44 wt. %. The molecular weight distribution of THF-soluble was measured to give the result that there were peaks at the positions of 0.4×10^4 and 7.0×10^4, with Mn = 0.58×10^4, Mw = 10×10^4, Mw/Mn = 17, and the molecular weights of 10^4 or lower being 21 wt. %. Further, Tg of the resin was 56°C, and the glass transition point Tg_1 of the components of 10^4 or less separated by GPC was 56°C.

Example 19

Into a reactor, 150 parts by weight of cumene was charged, and the temperature was raised to the reflux temperature. The following mixture was added dropwise under cumene reflux over 4 hours.

Monomer mixture	Formulated ratio
Styrene monomer	100 wt. parts
Di-tert-butylperoxide	4 "

Further, polymerization was completed under cumene reflux (146 - 156°C) and the cumene was removed. The styrene-n-butyl acrylate copolymer obtained had Mw = 6900, Mw/Mn = 2.3, a main peak at a molecular weight of 7100 and Tg = 75°C.

The above polystyrene (30 parts by weight) was dissolved in the following monomer mixture to provide a mixed solution.

Monomer mixture	Formulated ratio
Styrene monomer	52 wt. parts
n-Butyl acrylate monomer	18 "
Divinylbenzene	0.3 "
Benzoyl peroxide	1 "
tert-Butylperoxy-2-ethylhexanoate	1.6 "

Into the above mixture, 170 parts by weight of water containing 0.1 part by weight of a partially saponified polyvinyl alcohol dissolved therein was added to form a suspension. The above suspension was added into a reactor charged with 15 parts by weight of water and replaced with nitrogen, and the reaction was carried out at a temperature of 70 to 95°C for 6 hours. After completion of the reaction, the product was filtered, dehydrated and dried to give a composition of a styrene-n-butyl acrylate copolymer and a styrene-n-butyl methacrylate.

The content of the THF-insoluble in this composition was 30 wt. %. The molecular weight distribution of THF-soluble was measured to give the result that there were peaks at the positions of 0.75×10^4 and 4.3×10^4, with Mn = 0.65×10^4, Mw = 10×10^4, Mw/Mn = 15, and the molecular weights of 10^4 or lower being 18 wt. %. Further, Tg of the resin was 61°C, and the glass transition point Tg_1 of the components of 10^4 or less separated by GPC was 70°C.

Comparative Example 11

Monomer mixture	Formulated ratio
Styrene monomer	77 wt. parts
n-Butyl acrylate monomer	23 "
Divinylbenzene	0.4 "
Benzoyl peroxide	0.75 "
tert-Butylperoxy-2-ethylhexanoate	1.8 "

Into the above mixture, 170 parts by weight of water containing 0.1 part by weight of a partially saponified polyvinyl alcohol dissolved therein was added to form a suspension. The above suspension was added into a reactor charged with 15 parts by weight of water and replaced with nitrogen, and the reaction was carried out at a temperature of 70 to 95°C for 6 hours. After completion of the reaction, the product was filtered, dehydrated and dried to give a styrene-n-butyl acrylate copolymer.

The content of the THF-insoluble in this composition was 58 wt.%. The molecular weight distribution of THF-soluble was measured to give the result that there was only a peak at 4.0×10^4, with Mn = 1.4×10^4, Mw = 11×10^4, Mw/Mn = 8.

Comparative Example 12

Into a reactor, 200 parts by weight of cumene was charged, and the temperature was raised to the reflux temperature. To this was added dropwise a mixture of 100 parts by weight of styrene and 8 parts by weight of di-tert-butyl peroxide under cumene reflux over 4 hours. Further, polymerization was completed under cumene reflux (146 - 156°C) and cumene was removed. The polystyrene obtained had Mw = 3700, Mw/Mn = 2.64, a main peak at a molecular weight of 3500, and Tg = 57°C.

The above polystyrene (30 parts by weight) was dissolved in the following monomer mixture to provide a mixed solution.

Monomer mixture	Formulated ratio
Styrene monomer	54 wt. parts
n-Butyl acrylate monomer	16 "
Divinylbenzene	1.5 "
Benzoyl peroxide	1 "

Into the above mixture, 170 parts by weight of water containing 0.1 part by weight of a partially saponified polyvinyl alcohol dissolved therein was added to form a suspension. The above suspension was added into a reactor charged with 15 parts by weight of water and replaced with nitrogen, and the reaction was carried out at a temperature of 70 to 95°C for 6 hours. After completion of the reaction, the product was filtered, dehydrated and dried to give a composition of a polystyrene and a styrene-n-butyl acrylate copolymer.

The content of the THF-insoluble in this composition was 75 wt. %. The molecular weight distribution of THF-soluble was measured to give the result that there were peaks at the position of 0.34×10^4, with Mn = 0.21×10^4, Mw = 0.42×10^4, Mw/Mn = 2, and the molecular weights of 104 or lower being 18 wt. %. Further, Tg of the resin was 58°C, and the glass transition point Tg_1 of the components of 10^4 or less separated by GPC was 57°C.

Comparative Example 13

Into a reactor, 200 parts by weight of cumene was charged, and the temperature was raised to the reflux temperature. To this was added dropwise a mixture of 100 parts by weight of styrene and 8 parts by weight of di-tert-butylperoxide under cumene reflux over 4 hours. Further, polymerization was completed under cumene reflux (146 - 156°C) and cumene was removed. The polystyrene obtained had Mw = 5700, Mw/Mn = 2.65, a main peak at a molecular weight of 5300, and Tg = 56°C.

The above polystyrene (30 parts by weight) was dissolved in the following monomer mixture to provide a mixed solution.

Monomer mixture	Formulated ratio
Styrene monomer	54 wt. parts
n-Butyl acrylate monomer	16 "
Divinylbenzene	0.14 "
tert-Butylperoxy-2-ethylhexanoate	1.0 "

Into the above mixture, 170 parts by weight of water containing 0.1 part by weight of a partially saponified polyvinyl alcohol dissolved therein was added to form a suspension. The above suspension was added into a reactor charged with 15 parts by weight of water and replaced with nitrogen, and the reaction was carried out at a temperature of 70 to 95°C for 6 hours. After completion of the reaction, the product was filtered, dehydrated and dried to give a composition of a polystyrene and a styrene-n-butyl acrylate copolymer.

The content of the THF-insoluble in this composition was 30 wt. %. The molecular weight distribution of THF-soluble was measured to give the result that there were peaks at the positions of 0.4×10^4 and 15×10^4, with Mn = 0.60×10^4, Mw = 25×10^4, Mw/Mn = 42, and the molecular weights of 10^4 or lower being 22 wt. %. Further, Tg of the resin was 56°C, and the glass transition point Tg_1 of the components of 10^4 or less separated by GPC was 56°C.

Preparation Example 1

The resin composition of Example 15 (100 parts by weight), 60 parts by weight of a magnetic material, 4 parts by weight of a low molecular weight polypropylene and 2 parts by weight of a positive charge controller were thermally kneaded, and a toner was prepared by use of a micropulverizer and a classifying device.

The pulverizability of the toner starting material was very good, and the treated amount for obtaining a volume-average size as the pulverized particle size of 10 μ was a value of 15.3 kg/hr. Also, there was no sticking in the pulverizer.

A developer comprising 100 parts by weight of the toner mixed with 0.4 part by weight of a hydrophobic silica was charged into a copying machine (NP-5540 produced by Canon), and image quality and fixability were evaluated.

As the result of successive copying of 50000 sheets, stable and good images were formed. Further, fixability was also good, with good anti-offset characteristic and anti-winding characteristic. Further, there was no filming or sticking onto the photosensitive member.

Preparation Example 2

Preparation 1 was repeated except for using the resin composition of Example 16 to obtain substantially the same results as in Preparation Example 1.

Preparation Examples 3 - 5, Comparative Preparation Examples 1 - 4

Toners were prepared in the same manner as in Preparation Example 1 except for using the resin compositions of Examples 17, 18 and 19 (Preparation Examples 3 - 5). On the other hand, toners were prepared in the same manner as in Preparation Example 1 except for using the polystyrene used as the starting material for the resin composition in Example 15, and the resin compositions of Comparative Examples 11, 12 and 13,

respectively (Comparative Preparation Examples 1 - 4).

Evaluation methods

Pulverizability of the toner starting material was evaluated by the amount treated per unit time under an air pressure of 5.5 kg/cm^2 by a micropulverizer by use of jet air steam as a measure.

Fixability, anti-offset characteristic, anti-winding characteristic and image quality, successive copying characteristic were examined by use of a copying machine (NP-5540 produced by Canon K.K.).

Particularly, anti-offset characteristic was examined by lowering the set temperature in the fixer by 5°C, dismantling the cleaning mechanism in the fixing roller and observing whether the image was contaminated or the roller was contaminated.

Fixability was measured by rubbing the image with Silbon C paper reciprocally for 10 times under a load of about 100 g and representing the peeling of the image in terms of a lowering in percentage the reflective density. The evaluation of image was conducted on a 200-th sheet when successive copying of 200 sheets was conducted.

Anti-winding characteristic was measured by forming 3 sheets of the whole surface black image and by observing the trace of a pawl for peeling attached to the fixing roller remaining on the copies to judge how the peeling relied on the action of the pawl.

Table 6

	Pulverizability (kg/hr)	Sticking in pulverizer	Successive developing char.	Fixability	Anti-offset char.	Anti-winding char.
Preparation Example 1	Very good (15.3)	None	Good for 50000 sheets	Very good	Good	Good
" 2	" (14)	"	"	"	"	"
" 3	" (16)	"	"	"	"	"
" 4	Good (13.5)	"	"	Good	"	"
" 5	" (13.7)	"	"	"	"	"
Comparative Preparation Example 1*	Very good (25)	Observed	Troubled ** after 1000 sheets	Very good	Very bad	Very bad
" 2	Very poor (3)	None	Good for 50000 sheets	Very bad	Bad	Good
" 3	Very good (16.2)	"	Troubled ** after 10000 sheets	Bad	"	"
" 4	Very poor (5)	"	Good for 50000 sheets	Very bad	"	"

* : Slight filming on photosensitive member was also observed.

**: Image density remarkably lowered after the indicated number of sheets.

Claims

1. A toner for developing electrostatic latent images, comprising: a colorant or magnetic powder and a binder

resin; said binder resin having 10 to 60 wt.% of a chloroform-insoluble or THF (tetrahydrofuran)-insoluble and a chloroform-soluble or THF-soluble and comprising 10 to 50 wt.% of components having molecular weights of 10,000 or less, the chloroform-soluble or THF-soluble providing a molecular weight distribution in the chromatogram of GPC (gel permeation chromatography) thereof such that it provides a ratio (Mw/Mn) of weight-average molecular weight (Mw)/number-average molecular weight (Mn) ≧ 5, and there are at least one peak in the molecular weight range of 2,000 to 10,000 and at least one peak or shoulder in the range of 15,000 to 100,000.

2. A toner according to claim 1, wherein the binder resin comprises 40 to 90 wt.% of the chloroform-soluble or THF-soluble, the chloroform-soluble or THF-soluble of the binder resin comprising a vinyl type polymer.

3. A toner according to claim 2, wherein the binder resin comprises 10 to 50 wt.% of the chloroform-insoluble or THF-insoluble.

4. A toner according to claim 2, wherein the binder resin comprises 10 to 50 wt.% of the chloroform-insoluble or THF-insoluble, and the chloroform-soluble or THF-soluble of the binder resin provides a molecular weight distribution in the GPC chromatogram thereof such that there are a main peak in the molecular weight range of 2,000 to 15,000 and a sub-peak or shoulder in the molecular weight range of 8,000 to 80,000.

5. A toner according to claim 2, wherein the chloroform-soluble or THF-soluble of the binder resin comprises 0-20% of a component A having molecular weights of 500,000 or above, 10-60% of a component B having molecular weights of 30,000 to 500,000, and 20-90 wt.% of a component having molecular weights of 30,000 or less based on the areal ratio in the GPC chromatogram of the chloroform-soluble or THF-soluble.

6. A toner according to claim 5, wherein the chloroform-soluble or THF-soluble of the binder resin comprises 1 - 9% of the component A.

7. A toner according to claim 1, wherein the binder resin comprises 20 - 39 wt.% of the components having molecular weights of 10,000 or less.

8. A toner according to claim 1, wherein the chloroform-soluble or THF-soluble of the binder resin provides a ratio h_1/h_2 in the range of 0.4/1 to 4.0/1 in the GPC chromatogram thereof, wherein h_1 denotes a height of the highest peak in the molecular weight range of 2,000 to 10,000, and h_2 denotes the height of the highest peak in the molecular weight range of 15,000 to 100,000.

9. A toner according to claim 8, wherein the chloroform-soluble or THF-soluble of the binder resin has a number-average molecular weight of 2,000 to 9,000.

10. A toner according to claim 1, wherein the chloroform-soluble or THF-soluble provides, in the GPC chromatogram thereof, a peak in the molecular weight range of 2,000 to 8,000 and a peak or shoulder in the molecular weight range of 20,000 to 70,000.

11. A toner according to claim 1, wherein the chloroform-soluble or THF-soluble of the binder resin provides an Mw/Mn ratio in the range of 5 to 80.

12. A toner according to claim 11, wherein the chloroform-soluble or THF-soluble of the binder resin provides an Mw/Mn ratio in the range of 10 to 60.

13. A toner according to claim 1, wherein the chloroform-soluble or THF-soluble of the binder resin satisfies the following relationship:

$$Tg_1 \geqq Tg_t - 5,$$

wherein Tg_1 denotes a glass transition point (°C) of the components having molecular weights of 10,000 or less in the chloroform-soluble or THF-soluble and Tg_t denotes the glass transition point (°C) of the toner.

14. A toner according to claim 1, wherein the binder resin has been prepared by forming a first polymer which has a glass transition point of 50°C or higher and provides a molecular weight distribution thereof according to GPC such that there is a main peak in the molecular weight range of 2,000 to 10,000 and it provides a ratio (Mw/Mn) of weight-average molecular weight (Mw)/number-average molecular weight (Mn) ≦ 3.5;

and subjecting a polymerizable monomer with the first polymer dissolved therein to suspension polymerization.

15. A toner according to claim 14, wherein the binder resin comprises a crosslinked vinyl type polymer or copolymer.

16. A toner according to claim 14, wherein the first polymer comprises a non-crosslinked homopolymer or copolymer.

17. A toner according to claim 1, wherein the binder resin comprises styrene type homopolymer, styrene type copolymer, styrene-acrylate copolymer or styrene-methacrylate copolymer.

18. A process for producing a binder resin for a toner, comprising:

forming by solution polymerization a first polymer having a glass transition point of 50°C or higher and providing a molecular weight distribution thereof according to the GPC such that there is a main peak in the molecular weight range of 2,000 to 10,000 and it provides a ratio (Mw/Mn) of weight-average molecular weight (Mw)/number-average molecular weight (Mn) $\leqq$ 3.5;

dissolving the first polymer in a polymerizable monomer to formulate a monomer composition; and

subjecting the monomer composition to suspension polymerization, thereby to form a resin composition comprising 10 to 70 wt.% of a chloroform-insoluble or THF(tetra-hydrofuran)-insoluble and a chloroform-soluble or THF-soluble; the chloroform-soluble or THF-soluble providing a molecular weight distribution in the GPC chromatogram thereof such that it has a ratio Mw/Mn $\geqq$ 5; and there are at least one peak in the molecular weight range of 2,000 to 10,000 and at least one peak or shoulder in the molecular weight region of 15,000 to 100,000; and components having molecular weights of 10,000 or less are contained in a proportion of 10 - 50 wt.% of the total resin composition.

19. A process according to claim 18, wherein the first copolymer comprises a vinyl type homopolymer or copolymer.

20. A process according to claim 18, wherein the monomer composition contains a crosslinking agent.

21. A process according to claim 20, wherein the monomer composition contains a vinyl type monomer as the polymerizable monomer and a divinyl type monomer as the crosslinking agent.

22. A process according to claim 18, wherein the monomer composition comprises 10 to 120 parts by weight of the first polymer per 100 parts by weight of the polymerizable monomer.

23. A process according to claim 22, wherein the monomer composition comprises 20 to 100 parts by weight of the first polymer per 100 parts by weight of the polymerizable monomer.

24. A process according to claim 20, wherein the monomer composition contains the crosslinking agent in a proportion of 0.1 to 2.0 wt.% of the polymerizable monomer.

25. A process according to claim 18, wherein the solution polymerization is effected at a temperature of 70 to 180°C by using 0.1 wt. part or more of a polymerization initiator per 100 parts by weight of a polymerizable monomer.

26. A process according to claim 25, wherein the solution polymerization is effected by using 30 to 400 wt. parts of the polymerizable monomer per 100 parts by weight of a solvent.

27. A process according to claim 18, wherein the suspension polymerization is effected by using 100 parts by weight or less of the polymerizable monomer per 100 parts by weight of an aqueous dispersion medium.

28. A process according to claim 27, wherein the suspension polymerization is effected by using 10 - 90 parts by weight of the polymerizable monomer per 100 parts by weight of the aqueous dispersion medium.

29. A process according to claim 20, wherein the suspension polymerization is effected by using the monomer composition which comprises the crosslinking agent in a proportion of 0.1 to 2.0 wt.% of the polymerizable monomer and 0.5 to 10 parts by weight of a polymerization initiator per 100 parts by weight of the polymerizable monomer.

Patentansprüche

1. Toner zur Entwicklung elektrostatischer, latenter Bilder, umfassend: ein Färbemittel oder ein magnetisches Pulver und ein Bindeharz, wobei das Bindeharz 10 bis 60 Gew.-% eines chloroformunlöslichen oder THF-unlöslichen (tetrahydrofuranunlöslichen) Bestandteils und eines chloroformlöslichen oder THF-löslichen Bestandteils enthält und 10 bis 50 Gew.-% an Bestandteilen enthält, die Molekulargewichte von 10000 oder weniger aufweisen, wobei der chloroformlösliche oder THF-lösliche Bestandteil eine solche Molekulargewichtsverteilung in seinem GPC-Chromatogramm (Gelpermeationschromatogramm) aufweist, daß es ein Verhältnis (Mw/Mn), [gewichtsmittleres Molekulargewicht (Mw)] /[zahlenmittleres Molekulargewicht (Mn)], ≧ 5 bereitstellt und es wenigstens einen Peak im Molekulargewichtsbereich von 2000 bis 10000 und wenigstens einen Peak oder eine Schulter im Bereich von 15000 bis 100000 gibt.

2. Toner nach Anspruch 1, worin das Bindeharz 40 bis 90 Gew.-% des chloroformlöslichen oder THF-löslichen Bestandteils umfaßt, wobei der chloroformlösliche oder THF-lösliche Bestandteil des Bindeharzes ein Polymer vom Vinyltyp umfaßt.

3. Toner nach Anspruch 2, worin das Bindeharz 10 bis 50 Gew.-% des chloroformunlöslichen oder THF-unlöslichen Bestandteils umfaßt.

4. Toner nach Anspruch 2, worin das Bindeharz 10 bis 50 Gew.-% des chloroformunlöslichen oder des THF-unlöslichen Bestandteils umfaßt und der chloroformlösliche oder THF-lösliche Bestandteil des Bindeharzes eine solche Molekulargewichtsverteilung in seinem GPC-Chromatogramm bereitstellt, daß es einen Hauptpeak im Molekulargewichtsbereich von 2000 bis 15000 und einen Nebenpeak oder eine Schulter im Molekulargewichtsbereich von 8000 bis 80000 gibt.

5. Toner nach Anspruch 2, worin der chloroformlösliche oder THF-lösliche Bestandteil des Bindeharzes 0 bis 20% einer Komponente A mit Molekulargewichten von 500000 oder darüber, 10 bis 60% einer Komponente B mit Molekulargewichten von 30000 bis 500000 und 20 bis 90 Gew.-% einer Komponente mit Molekulargewichten von 30000 oder weniger umfaßt, bezogen auf das Flächenverhältnis im GPC-Chromatogramm des chloroformlöslichen oder THF-löslichen Bestandteils.

6. Toner nach Anspruch 5, worin der chloroformlösliche oder THF-lösliche Bestandteil des Bindeharzes 1 bis 9% der Komponente A umfaßt.

7. Toner nach Anspruch 1, worin der Bindeharz 20 bis 39 Gew.-% der Komponenten umfaßt, die Molekulargewichte von 10000 oder weniger aufweisen.

8. Toner nach Anspruch 1, worin der chloroformlösliche oder THF-lösliche Bestandteil des Bindeharzes ein Verhältnis h_1/h_2 im Bereich von 0,4/1 bis 4,0/1 in seinem GPC-Chromatogramm aufweist, worin h_1 eine Höhe des höchsten Peaks im Molekulargewichtsbereich von 2000 bis 10000 und h_2 die Höhe des höchsten Peaks im Molekulargewichtsbereich von 15000 bis 100000 bedeuten.

9. Toner nach Anspruch 8, worin der chloroformlösliche oder THF-lösliche Bestandteil des Bindeharzes ein zahlenmittleres Molekulargewicht von 2000 bis 9000 aufweist.

10. Toner nach Anspruch 1, worin der chloroformlösliche oder THF-lösliche Bestandteil in seinem GPC-Chromatogramm einen Peak im Molekulargewichtsbereich von 2000 bis 8000 und einen Peak oder eine Schulter im Molekulargewichtsbereich von 20000 bis 70000 bereitstellt.

11. Toner nach Anspruch 1, worin der chloroformlösliche oder THF-lösliche Bestandteil des Bindeharzes ein Mw/Mn-Verhältnis im Bereich von 5 bis 80 bereitstellt.

12. Toner nach Anspruch 11, worin der chloroformlösliche oder THF-lösliche Bestandteil des Bindeharzes ein Mw/Mn-Verhältnis im Bereich von 10 bis 60 bereitstellt.

13. Toner nach Anspruch 1, worin der chloroformlösliche oder THF-lösliche Bestandteil des Bindeharzes die folgende Beziehung erfüllt:

$$Tg_1 \geqq Tg_t - 5$$

worin Tg_1 einen Glasübergangspunkt (in °C) der Komponenten darstellt, die Molekulargewichte von 10000 oder weniger im chloroformlöslichen oder THF-löslichen Bestandteil aufweisen, und Tg_t den Glasüber-

* C L M S *

gangspunkt (in °C) des Toners darstellt.

14. Toner nach Anspruch 1, worin das Bindeharz hergestellt wurde, indem
    - ein erstes Polymer gebildet wird, das einen Glasübergangspunkt von 50°C oder mehr aufweist und eine solche Molekulagewichtsverteilung gemäß GPC bereitstellt, daß es einen Hauptpeak in der Molekulargewichtsbereich von 2000 bis 10000 gibt, und daß sie ein Verhältnis (Mw/Mn), [gewichtsmittleres Molekulargewicht (Mw)]/[zahlenmittleres Molekulargewicht (Mn)], ≦ 3,5 bereitstellt, und dann
    - ein polymerisierbares Monomer, in dem das erste Polymer gelöst ist, einer Suspensionspolymerisation unterworfen wird.

15. Toner nach Anspruch 14, worin das Bindeharz ein Polymer oder Copolymer vom quervernetzten Vinyltyp umfaßt.

16. Toner nach Anspruch 14, worin das erste Polymer ein nicht quervernetztes Homopolymer oder Copolymer umfaßt.

17. Toner nach Anspruch 1, worin das Bindeharz ein Homopolymer vom Styroltyp, ein Copolymer vom Styroltyp, ein Copolymer aus Styrol und Acrylat oder ein Copolymer aus Styrol und Methacrylat umfaßt.

18. Verfahren zur Herstellung eines Bindeharzes für einen Toner, umfassend:
    - Bilden eines ersten Polymers durch Lösungspolymerisation, das einen Glasübergangspunkt von 50°C oder mehr besitzt und eine solche Molekulargewichtsverteilung gemäß GPC bereitstellt, daß es einen Hauptpeak im Molekulargewichtsbereich von 2000 bis 10000 gibt, und daß sie ein Verhältnis (Mw/Mn), [gewichtsmittleres Molekulargewicht (Mw)]/[zahlenmittleres Molekulargewicht (Mn)], ≦ 3,5 aufweist,
    - Auflösen des ersten Polymers in einem polymerisierbaren Monomer zur Bildung einer Monomerzusammensetzung, und
    - Unterwerfen der Monomerzusammensetzung einer Suspensionspolymerisation, wodurch eine Harzzusammensetzung gebildet wird, die 10 bis 70 Gew.-% eines chloroformunlöslichen oder THF-unlöslichen (tetrahydrofuranunlöslichen) Bestandteils und eines chloroformlöslichen oder THF-löslichen Bestandteils umfaßt, wobei der chloroformlösliche oder THF-lösliche Bestandteil eine solche Molekulargewichtsverteilung in seinem GPC-Chromatogramm bereitstellt, daß sie ein Verhältnis Mw/Mn ≧ 5 aufweist, und daß es wenigstens einen Peak im Molekulargewichtsbereich von 2000 bis 10000 und wenigstens einen Peak oder eine Schulter im Molekulargewichtsbereich von 15000 bis 100000 gibt, und daß Komponenten mit Molekulargewichten von 10000 oder weniger in einem Anteil von 10 bis 50 Gew.-% enthalten sind, bezogen auf die gesamte Harzzusammensetzung.

19. Verfahren nach Anspruch 18, worin das erste Copolymer ein Homopolymer oder Copolymer vom Vinyltyp umfaßt.

20. Verfahren nach Anspruch 18, worin die Monomerzusammensetzung ein Quervernetzungsmittel enthält.

21. Verfahren nach Anspruch 20, worin die Monomerzusammensetzung ein Monomer vom Vinyltyp als polymerisierbares Monomer und ein Monomer vom Divinyltyp als Quervernetzungsmittel umfaßt.

22. Verfahren nach Anspruch 18, worin die Monomerzusammensetzung 10 bis 120 Gewichtsteile des ersten Polymers auf 100 Gewichtsteile des polymerisierbaren Monomers umfaßt.

23. Verfahren nach Anspruch 22, worin die Monomerzusammensetzung 20 bis 100 Gewichtsteile des ersten Polymers auf 100 Gewichtsteile des polymerisierbaren Monomers umfaßt.

24. Verfahren nach Anspruch 20, worin die Monomerzusammensetzung das Quervernetzungsmittel in einem Anteil von 0,1 bis 2,0 Gew.-% des polymerisierbaren Monomers enthält.

25. Verfahren nach Anspruch 18, worin die Lösungspolymerisation bei einer Temperatur von 70 bis 180°C durchgeführt wird unter Verwendung von 0,1 Gewichtsteilen oder mehr eines Polymerisationsinitiators auf 100 Gewichtsteile eines polymerisierbaren Monomers.

26. Verfahren nach Anspruch 25, worin die Lösungspolymerisation durchgeführt wird unter Verwendung von 30 bis 400 Gewichtsteilen des polymerisierbaren Monomers auf 100 Gewichtsteile eines Lösungsmittels.

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27. Verfahren nach Anspruch 18, worin die Suspensionspolymerisation durchgeführt wird unter Verwendung von 100 Gewichtsteilen oder weniger des polymerisierbaren Monomers auf 100 Gewichtsteile eines wäßrigen Dispersionsmaterials.

28. Verfahren nach Anspruch 27, worin die Suspensionspolymerisation durchgeführt wird unter Verwendung von 10 bis 90 Gewichtsteilen des polymerisierbaren Monomers auf 100 Gewichtsteile des wäßrigen Dispersionsmaterials.

29. Verfahren nach Anspruch 20, worin die Suspensionspolymerisation unter Verwendung der Monomerzusammensetzung durchgeführt wird, die das Quervernetzungsmittel in einem Anteil von 0,1 bis 2,0 Gew.-% des polymerisierbaren Monomers und 0,5 bis 10 Gewichtsteilen eines Polymerisationsinitiators auf 100 Gewichtsteile des polymerisierbaren Monomers umfaßt.

Revendications

1. Toner pour le développement d'images latentes électrostatiques, comprenant : un colorant ou une poudre magnétique et une résine servant de liant ; ladite résine servant de liant renfermant de 10 à 60 % en poids d'une matière insoluble dans le chloroforme ou insoluble dans le THF (tétrahydrofuranne) et une matière soluble dans le chloroforme ou le THF et comprenant 10 à 50 % en poids de constituants ayant des poids moléculaires égaux ou inférieurs à 10 000, la matière soluble dans le chloroforme ou soluble dans le THF engendrant une distribution des poids moléculaires dans le chromatogramme de CPG (chromatographie de perméation sur gel) de cette matière, telle qu'elle donne un rapport (Mp/Mn) de la moyenne pondérale du poids moléculaire (Mp) à la moyenne numérique du poids moléculaire (Mn) supérieur ou égal à 5, avec au moins un pic dans la plage des poids moléculaires de 2000 à 10 000 et au moins un pic ou épaulement dans la plage de 15 000 à 100 000.

2. Toner suivant la revendication 1, dans lequel la résine servant de liant comprend 40 à 90 % en poids de la matière soluble dans le chloroforme ou soluble dans le THF, la matière soluble dans le chloroforme ou soluble dans le THF de la résine servant de liant comprenant un polymère de type vinylique.

3. Toner suivant la revendication 2, dans lequel la résine servant de liant comprend 10 à 50 % en poids de la matière insoluble dans le chloroforme ou insoluble dans le THF.

4. Toner suivant la revendication 2, dans lequel la résine servant de liant comprend 10 à 50 % en poids de la matière insoluble dans le chloroforme ou insoluble dans le THF, et la matière soluble dans le chloroforme ou soluble dans le THF de la résine servant de liant donne une distribution des poids moléculaires dans son chromatogramme de CPG telle qu'il existe un pic principal dans la plage des poids moléculaires de 2000 à 15 000 et un pic secondaire ou épaulement dans la plage des poids moléculaires de 8000 à 80 000.

5. Toner suivant la revendication 2, dans lequel la matière soluble dans le chloroforme ou soluble dans le THF de la résine servant de liant comprend 0 à 20 % d'un constituant A ayant des poids moléculaires égaux ou supérieurs à 500 000, 10 à 60 % d'un constituant B ayant des poids moléculaires de 30 000 à 500 000, et 20 à 90 % en poids d'un constituant ayant des poids moléculaires égaux ou inférieurs à 30 000 sur la base du rapport des surfaces dans le chromatogramme de CPG de la matière soluble dans le chloroforme ou soluble dans le THF.

6. Toner suivant la revendication 5, dans lequel la matière soluble dans le chloroforme ou soluble dans le THF de la résine servant de liant comprend 1 à 9 % du constituant A.

7. Toner suivant la revendication 1, dans lequel la résine servant de liant comprend 20 à 39 % en poids des constituants ayant des poids moléculaires égaux ou inférieurs à 10 000.

8. Toner suivant la revendication 1, dans lequel la matière soluble dans le chloroforme ou soluble dans le THF de la résine servant de liant donne un rapport h_1/h_2 compris dans l'intervalle de 0,4/1 à 4,0/1 dans son chromatogramme de CPG, h_1 désignant la hauteur du pic le plus haut dans la plage des poids moléculaires de 2000 à 10 000 et h_2 désignant la hauteur du pic le plus haut dans la plage des poids moléculaires de 15 000 à 100 000.

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9. Toner suivant la revendication 8, dans lequel la matière soluble dans le chloroforme ou soluble dans le THF de la résine servant de liant possède une moyenne numérique du poids moléculaire de 2000 à 9000.

10. Toner suivant la revendication 1, dans lequel la matière soluble dans le chloroforme ou soluble dans le THF donne, dans son chromatogramme de CPG, un pic dans la plage des poids moléculaires de 2000 à 8000 et un pic ou épaulement dans la plage des poids moléculaires de 20 000 à 70 000.

11. Toner suivant la revendication 1, dans lequel la matière soluble dans le chloroforme ou soluble dans le THF de la résine servant de liant donne un rapport Mp/Mn compris dans l'intervalle de 5 à 80.

12. Toner suivant la revendication 11, dans lequel la matière soluble dans le chloroforme ou soluble dans le THF de la résine servant de liant donne un rapport Mp/Mn compris dans l'intervalle de 10 à 60.

13. Toner suivant la revendication 1, dans lequel la matière soluble dans le chloroforme ou soluble dans le THF de la résine servant de liant satisfait la relation suivante

$$Tg_1 \geqq Tg_t - 5,$$

dans laquelle Tg_1 représente le point de transition vitreuse (°C) des constituants ayant des poids moléculaires égaux ou inférieurs à 10 000 dans la matière soluble dans le chloroforme ou soluble dans le THF et Tg_t représente le point de transition vitreuse (°C) du toner.

14. Toner suivant la revendication 1, dans lequel la résine servant de liant a été préparée en formant un premier polymère qui possède un point de transition vitreuse égal ou supérieur à 50°C et qui présente une distribution des poids moléculaires par CPG telle qu'il existe un pic principal dans la plage des poids moléculaires de 2000 à 10 000 et qu'il engendre un rapport (Mp/Mn) de la moyenne pondérale du poids moléculaire (Mp) à la moyenne numérique du poids moléculaire (Mn) inférieur ou égal à 3,5 ; et en soumettant un monomère polymérisable, avec le premier polymère dissous dans ce monomère, à une polymérisation en suspension.

15. Toner suivant la revendication 14, dans lequel la résine servant de liant comprend un polymère ou copolymère de type vinylique réticulé.

16. Toner suivant la revendication 14, dans lequel le premier polymère comprend un homopolymère ou copolymère non réticulé.

17. Toner suivant la revendication 1, dans lequel la résine servant de liant comprend un homopolymère du type styrène, un copolymère du type styrène, un copolymère styrène-acrylate ou un copolymère styrène-méthacrylate.

18. Procédé de production d'une résine servant de liant pour un toner, comprenant les étapes consistant :

à former par polymérisation en solution un premier polymère ayant un point de transition vitreuse égal ou supérieur à 50°C et présentant une distribution des poids moléculaires par CPG telle qu'il existe un pic principal dans la plage des poids moléculaires de 2000 à 10 000 et qu'il donne un rapport (Mp/Mn) de la moyenne pondérale du poids moléculaire (Mp) à la moyenne numérique du poids moléculaire (Mn) inférieur ou égal à 3,5 ;

à dissoudre le premier polymère dans un monomère polymérisable pour formuler une composition de monomères ; et

à soumettre la composition de monomères à une polymérisation en suspension, pour former ainsi une composition de résine comprenant 10 à 70 % en poids d'une matière insoluble dans le chloroforme ou insoluble dans le THF (tétrahydrofuranne) et d'une matière soluble dans le chloroforme ou soluble dans le THF ; la matière soluble dans le chloroforme ou soluble dans le THF donnant une distribution des poids moléculaires dans son chromatogramme de CPG telle qu'elle possède un rapport Mp/Mn supérieur ou égal à 5, et qu'il existe au moins un pic dans la plage des poids moléculaires de 2 000 à 10 000 et au moins un pic ou épaulement dans la plage des poids moléculaires de 15 000 à 100 000 ; des constituants ayant des poids moléculaires égaux ou inférieurs à 10 000 étant présents en une proportion de 10 à 50 % en poids de la composition de résine totale.

19. Procédé suivant la revendication 18, dans lequel le premier copolymère comprend un homopolymère ou copolymère de type vinylique.

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20. Procédé suivant la revendication 18, dans lequel la composition de monomères contient un agent de réticulation.

21. Procédé suivant la revendication 20, dans lequel la composition de monomères contient un monomère de type vinylique comme monomère polymérisable et un monomère de type divinylique comme agent de réticulation.

22. Procédé suivant la revendication 18, dans lequel la composition de monomères comprend 10 à 120 parties en poids du premier polymère pour 100 parties en poids du monomère polymérisable.

23. Procédé suivant la revendication 22, dans lequel la composition de monomères comprend 20 à 100 parties en poids du premier polymère pour 100 parties en poids du monomère polymérisable.

24. Procédé suivant la revendication 20, dans lequel la composition de monomères contient l'agent de réticulation en une proportion de 0,1 à 2,0 % en poids du monomère polymérisable.

25. Procédé suivant la revendication 18, dans lequel la polymérisation en solution est effectuée à une température de 70 à 180°C en utilisant une quantité égale ou supérieure à 0,1 partie en poids d'un initiateur de polymérisation pour 100 parties en poids d'un monomère polymérisable.

26. Procédé suivant la revendication 25, dans lequel la polymérisation en solution est effectuée en utilisant 30 à 400 parties en poids du monomère polymérisable pour 100 parties en poids d'un solvant.

27. Procédé suivant la revendication 18, dans lequel la polymérisation en suspension est effectuée en utilisant une quantité égale ou inférieure à 100 parties en poids du monomère polymérisable pour 100 parties en poids d'un milieu aqueux de dispersion.

28. Procédé suivant la revendication 27, dans lequel la polymérisation en suspension est effectuée en utilisant 10 à 90 parties en poids du monomère polymérisable pour 100 parties en poids du milieu aqueux de dispersion.

29. Procédé suivant la revendication 20, dans lequel la polymérisation en suspension est effectuée en utilisant la composition de monomères qui comprend l'agent de réticulation en une proportion de 0,1 à 2,0 % en poids du monomère polymérisable et une proportion de 0,5 à 10 parties en poids d'un initiateur de polymérisation pour 100 parties en poids du monomère polymérisable.