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⑤④ **Toner and process for preparation thereof.**

⑤⑦ A toner comprising spherical particles obtainable by suspension polymerization which comprise a binder resin and a coloring agent, wherein the median diameter of the particles based on the volume is in the range of from 3 to 20 μm , the molecular weight distribution of the particles has a plurality of peaks such that the peak of the minimum position in the molecular weight distribution is lower than 50,000 and the peak of the maximum position is higher than 200,000, and processes for its production. The toner has excellent fixing properties, antiblocking properties and offset resistance.

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TONER AND PROCESS FOR PREPARATION THEREOF

Background of the Invention

(1) Field of the Invention

The present invention relates to a toner for use in the electrophotography. More particularly, the present invention relates to a toner showing excellent fixing property and offset resistance at the development and a process for the preparation of this toner.

(2) Description of the Prior Art

Toners used in the field of the electrophotography are composed of particles comprising a binder resin, a coloring agent and, if necessary, a charge-controlling agent and a magnetic material. The developing characteristic, the fixing property to a transfer sheet and the offset resistance can be mentioned as functions generally required for toners.

As the means for improving the fixing property and offset resistance in toners, there have been adopted a method in which a low-molecular-weight hydrogenated polybutadiene is incorporated in the binder resin (see Japanese Unexamined Patent Publication No.60-103354), a method in which a reactive prepolymer is incorporated into the binder resin (see Japanese Unexamined Patent Publication No. 56-110948), a method in which the ratio between styrene and 2-ethylmethahexyl methacrylate in the binder resin is controlled within a certain range (Japanese Unexamined Patent Publication No.60-57855), and a method for preparing toners in which polymerization initiators differing in the half-value period are used in the suspension polymerization and the ratio of the half-value period between the polymerization initiators is controlled within a certain range (see Japanese Examined Patent Publication No.64-11941). Toners prepared according to these methods have an excellent offset resistance and an excellent antiblocking property.

However, even if a low-molecular-weight resin is merely incorporated (made present) in toner particles, the fixing property is not sufficiently improved, and sometimes, a problem of a poor offset resistance is caused at the fixing step. Moreover, the durability of the toner per se is still insufficient and the additives such as the coloring agent, falling from the toner particles during the copying operation, degrade the developing characteristic. Similar defects are observed when the constituent ratio in the binder resin is specified. Although a fixing roller is maintained at a certain temperature at the development, the state of heating the toner particles is not always uniform. When the heating conditions of the fixing roller are delicately changed during the development, the viscosity of the binder resin is changed in the toner, resulting in changes of the penetrability and cohesiveness. Accordingly, the fixing property and offset resistance are degraded and hot offset or cold offset is sometimes caused. Therefore, further improvements of toners are required.

Summary of the Invention

Under this background, it is a primary object of the present invention to provide a toner in which a low-molecular-weight component imparting a sufficient fixing property and a high-molecular-weight component imparting offset resistance and blocking resistance are contained in an optimum state in a binder resin and particles are spherized to increase the mechanical strength, and a process for the preparation of this toner.

Another object of the present invention is to provide a toner in which the viscosity is not greatly changed when the toner is fused at the fixing step and which is excellent in the fixing property, offset resistance and apparatus adaptability, and a process for the preparation of this toner.

In accordance with the present invention, there is provided a toner consisting of spherical particles formed by suspension polymerization and comprising a binder resin and a coloring agent, wherein the median diameter based on the volume is in the range of from 3 to 20 μm , the molecular weight distribution has a plurality of peaks, the peak of the minimum position in the molecular weight distribution is at a position of a molecular weight lower than 50,000 and the peak of the maximum position is at a position higher than 200,000.

The occupancy ratio of a high-molecular-weight component having a molecular weight higher than the maximum peak value can be in the range of from 10 to 40% based on the entire particles. A releasing substance can be incorporated into the suspension polymerization particles.

In accordance with the present invention, there is provided a toner satisfying the above-mentioned requirements, which is further characterized in that in the temperature range of from 100 to 150°C at which the toner is heated fixing step, the temperature difference required for the viscosity of the toner to change from 5×10^6

poise to 5×10^4 poise under heating is at least 32°C.

The binder resin of the above-mentioned toner can have such flow characteristics that the flow-initiating temperature T_i satisfies the requirement of $(T_i - T_g) \leq 50$ in which T_g represents the glass transition temperature of the binder resin, and the temperature T_m for flow-out of 1/2 of the toner satisfies the requirement of $(T_m - T_i) \geq 30$.

Furthermore, the advantage viscosity gradient (absolute value) of the toner of the present invention in the temperature range of from 100 to 150°C is preferably 0.02 to 0.7/°C, and in this temperature region, there is preferably present at least one region where the absolute value of the viscosity gradient is smaller than 0.03/°C.

Furthermore, there are present two regions where the absolute value of the viscosity gradient is smaller than 0.03/°C, and these two regions can be a region of from 115 to 125°C and a region of from 130 to 140°C. Moreover, in the above-mentioned temperature range, the proportion of a region where the viscosity gradient is gentler than the average viscosity gradient is preferably at least 10%.

In accordance with the present invention, there is provided a process for the preparation of a toner by suspension polymerization using a vinyl monomer and a coloring agent, characterized in that an initiator having a half-value period of up to 30 minutes and a crosslinking agent are incorporated at the polymerization of said vinyl monomer and the polymerization is carried out so that the molecular weight distribution has a plurality of peaks.

The process of the present invention can be further characterized in that a releasing substance is incorporated in addition to the initiator and crosslinking agent at the polymerization of said vinyl monomer, at least two initiators differing in the half-value period and the crosslinking agent are incorporated at the polymerization of said vinyl monomer, the half-value period of at least one initiator is up to 20 minutes, and the polymerization is carried out so that the molecular weight distribution has a plurality of peaks.

According to the present invention, the polymerization can be carried out by incorporating at least one member selected from the group consisting of coloring agents, charge-controlling agents and magnetic materials in addition to said vinyl monomer and coloring agent.

According to the present invention, the polymerization can be carried out so that of a plurality of peaks of the molecular weight distribution, the minimum molecular weight peak is at a position of a molecular weight lower than 50,000 and a maximum molecular weight peak is at a position of a molecular weight higher than 200,000.

Incidentally, the viscosity gradient of the toner represents the ratio of the logarithm of the viscosity to the temperature. The change quantity of the viscosity to the temperature difference, $(X + \Delta) - X^\circ\text{C}$, is $\log(Y + \Delta)$ poise - $\log Y$ poise, and the viscosity gradient K is the value represented by the following formula :

$$K = (\log(Y + \Delta) - \log Y) / \Delta^\circ\text{C} \\ = (\log(Y + \Delta) / Y) / \Delta^\circ\text{C}$$

Incidentally, K monotonously decreases as the temperature is elevated, and the viscosity is the value measured by a flow tester.

Brief Description of the drawings

Fig. 1 is a characteristic curve illustrating the relation between the temperature and the change of the viscosity in toner particles of the present invention.

Fig. 2 through 4 are characteristic curves illustrating the molecular weight distributions of toner particles of the present invention.

Detailed Description of the Preferred Embodiments

According to the present invention, a binder resin comprising a low-molecular-weight component and a high-molecular weight component, which can be clearly distinguished from each other, is formed by using a polymerization initiator having a short half-value period and a cross-linking agent in the suspension polymerization, and the present invention is based on the finding that if these components are made present in the state where blocking is hardly caused while a coloring agent is being included, a toner consisting of polymer particles having excellent fixing property and offset resistance is obtained.

The toner of the present invention consists of spherical toner particles obtained by suspension polymerization, and it is important that the median diameter based on the volume of the toner particles should be in the range of from 3 to 20 μm and the molecular weight distribution should have a plurality of peaks. The median diameter of the toner particles is adjusted at the suspension polymerization, and formation of a plurality of peaks of the polymerization is accomplished by using an initiator having a short half-value period and a crosslinking agent at the suspension polymerization. In principle, the medial diameter D_{50} of the toner of the present inven-

tion is in the range of from 3 to 20 μm , especially from 5 to 13 μm , and particles having such a median diameter form an excellent toner, and at the development, scattering of the toner or fogging can be reduced. Moreover, these particles have a shape very similar to a shape of a true sphere and the toner has a good flowability.

Of a plurality of peaks of the molecular weight distribution, the molecular weight of the minimum peak (not the minimum volume but the minimum peak position) should be lower than 50,000, preferably 3,000 to 50,000, especially preferably 5,000 to 40,000, and the molecular weight of the maximum peak should be higher than 200,000, preferably 200,000 to 7,000,000, especially preferably 300,000 to 5,000,000. If low-molecular-weight and high-molecular-weight components are present with such a molecular weight distribution in the toner particles, when the toner is heated by a fixing roller or the like, the low-molecular-weight component is fused to sufficiently penetrate in a transfer sheet, whereby the fixing property of the toner is improved. The high-molecular-weight component is mixed in a good state with the low-molecular-weight component at the suspension polymerization and a certain and uniform cohesiveness is given to the entire binder resin without blocking or the like, whereby the offset resistance is improved.

In the present invention, it is preferred that the proportion of a high-molecular-weight component having a molecular weight higher than the above-mentioned maximum peak value be in the range of from 10 to 40%. If the high-molecular-weight component is present at such a proportion in the toner, sufficient viscosity and cohesiveness are maintained in the entire toner particles, and sufficient offset resistance is attained.

In addition to the above-mentioned structural features of the toner particles, the following requirement should be satisfied in the present invention. Namely, in the temperature region of from 100 to 150°C at which the toner is heated at the fixation, the temperature difference required for the viscosity of the toner to change from 5×10^6 poise to 5×10^4 poise should be at least 32°C, especially at least at 35°C. Fig. 1 is a characteristic curve showing the relation between the temperature and the viscosity in the toner of the present invention. In Fig. 1, the temperature is plotted on the abscissa and the logarithm of the viscosity is plotted on the ordinate. As is seen from the viscosity change curve A of the toner of the present invention in Fig. 1, 40°C is necessary for the viscosity to change from 5×10^6 poise to 5×10^4 poise while this temperature is smaller than 30°C in the curve of the conventional toner, and the gradient of the curve A of the toner of the present invention is considerably gentle. Namely, in the conventional toner, in order to change the viscosity from 5×10^6 poise to 5×10^4 poise, it is sufficient if the temperature is elevated only by less than 30°C, but in case of the toner of the present invention, the temperature should be elevated by at least 40°C.

The fact that the viscosity gradient of the toner is gentle in the above-mentioned temperature range indicates that the viscosity of the toner is substantially maintained at a constant level even if the heating state differs to some extent at the fixation or even if the melted state of the toner differs to some extent. It has been surprisingly found that if there is no substantial change of the viscosity as mentioned above, hot offset and cold offset can be generally prevented.

Furthermore, in the present invention, it is preferred that in the temperature range of from 100 to 150°C, the average viscosity gradient of the toner be 0.02 to 0.07/°C, and there be present at least one region where the viscosity gradient (absolute value) of the toner is smaller than 0.030/°C, especially smaller than 0.026/°C. As shown in Fig. 1, in the viscosity change curve A of the toner of the present invention, in the temperature range of from 115 to 125°C, the gradient (absolute value) is 0.014/°C and in the temperature range of from 130 to 140°C, the gradient is 0.025/°C. In contrast, in the viscosity change curve B of the conventional toner, throughout the temperature range of from 100 to 150°C, the viscosity gradient is larger than 0.05/°C. The toner particles of the present invention include ranges of a small gradient, and therefore, when the toner is heated by the fixing roller, no change of the viscosity is caused by the viscosity is maintained at a predetermined level. However, in the conventional toner, that is, a toner having a viscosity gradient larger than 0.05/°C, the change of the viscosity is conspicuous. This difference at the time of heating has serious influences on the penetrability, cohesiveness and anchoring effect which are factors having influences on the fixing property and offset resistance.

At the fixing step, the toner is heated for a short time by the fixing roller maintained at about 180°C. By this heating, the toner begins to melt at about 100°C, and in an appropriate fused state, the resin penetrates into a transfer sheet and when the fixing roller separates, the resin is left in the transfer sheet by dint of a certain cohesive force and an anchoring effect. In this case, it is understood that components having different physical properties are present in the binder resin, and it is considered that in the temperature range of a steep viscosity gradient of the toner, the component of the binder resin reducing the viscosity of the entire toner under elevation of the temperature acts and in the temperature region of a gentle gradient of the viscosity, the melted state is changed by elevation of the temperature but the component of the binder resin not substantially changing the viscosity characteristics of the entire toner acts.

In the present invention, it is preferred that as shown in Fig. 1, there be present two regions where the viscosity gradient is gentler than 0.030 poise/°C. For example, a first region can be present at temperatures of

from 115 to 125°C and a second region can be present at temperatures of from 130 to 140°C. A toner having such viscosity characteristics has a good apparatus adaptability and shows an excellent cohesiveness when the fixing roller in which the temperature delicately changes separates, with the result that the penetrability in a transfer sheet and the fixing property are improved. Accordingly, the fixed toner is not separated from the transfer sheet and contamination or offset is not found on the fixing roller.

In this toner, it is preferred that requirements of $(T_i - T_g) \leq 50$ and $(T_m - T_i) \geq 30$ be established among the temperature T_i of initiation of flow-out of the toner, the temperature T_m for flow-out of 1/2 of the toner and the glass transition temperature T_g of the binder resin. $(T_i - T_g)$ has a relation to the meltability of the toner particles and the penetrability in a transfer sheet and $(T_m - T_i)$ has a relation to the melted state of the toner and the viscosity of the toner.

If it is tried to reduce the difference $(T_i - T_g)$, also the difference $(T_m - T_i)$ tends to become small (see Table 4). In the toner particles of the present invention, however, by selecting a specific polymerization state and a specific resin, it becomes possible to maintain T_i within the above-mentioned range and especially satisfy the requirements of $(T_i - T_g) \leq 45$ and $(T_m - T_i) \geq 35$. If T_i is within the above-mentioned range, the difference $(T_i - T_g)$ of the toner particles is small and the toner particles are easily melted, and the penetration of the toner in a transfer sheet is accelerated. Furthermore, since the difference $(T_m - T_i)$ is large, the mixed state of the melt and the unmelted substance is kept for a long time and the viscosity of the toner is maintained at a relatively high level. Accordingly, offset to the fixing roller or the like is prevented and the anchoring effect to the transfer sheet is maintained.

In the present invention, a polymerization initiator having a half-value period of up to 30 minutes and a crosslinking agent are used at the suspension polymerization, or a plurality of polymerization initiators, at least one of which has a half-value period of up to 20 minutes, are used at the suspension polymerization, and low-molecular-weight and high-molecular-weight components of the binder resin are made present in the state where blocking is hardly caused, whereby good fixing property and offset resistance can be imparted to the toner particles. Moreover, a releasing agent is incorporated into the binder resin, whereby there can be provided a toner capable of preventing contamination of the surface of a roller used as the fixing means even in the case where there is a risk of incorporation of a relatively large amount of a low-molecular-weight component such as coloring agent into toner particles.

If a vinyl monomer is suspension-polymerized in the presence of a polymerization initiator having a half-value period of up to 30 minutes, especially up to 20 minutes, the majority of the polymerization initiator is deactivated at the initial stage of the polymerization and the polymerization is stopped in the state where the polymerization degree is low, with the result that a polymer having a low molecular weight is obtained. Simultaneously with the above reaction, the molecular weight is increased in a part of the polymerization reaction product by the crosslinking agent. Furthermore, after the violent reaction, the polymerization reaction is further advanced by the residual active initiator or by another initiator when a plurality of initiators is used. The obtained high-molecular-weight polymer is present in the state where the high molecular-weight polymer is mixed with the low-molecular-weight polymer obtained by the above reaction so that blocking is not caused, whereby a toner polymer is formed. If the crosslinking agent and the polymerization initiator having a short half-value period are added, conditions for forming a plurality of peaks, that is, a high-molecular-weight peak and a low-molecular-weight peak, can be set and a low-molecular-weight polymer is made present assuredly in the polymerization product (see Figs. 2 through 4).

In order to obtain a toner polymer having these peaks values, it is important that the crosslinking agent should be incorporated in an amount of 0.3 to 10 parts by weight, especially 0.5 to 8 parts by weight, per 100 parts by weight of the vinyl monomer. If the amount of the crosslinking agent is too large and exceeds the above-mentioned range, the fixing property of the toner particles is degraded, and if the amount of the crosslinking agent is too small, the offset resistance and blocking resistance are degraded.

The viscosity characteristics of the toner of the present invention can be attained by selecting the binder resin components satisfying the above-mentioned molecular weight distribution requirements of the binder resin by the suspension polymerization.

The materials used in the present invention and the suspension polymerization will now be described.

Materials Used

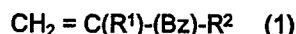
(a) Vinyl monomer

In the polymerization process of the present invention, at least one monomer having an ethylenically unsaturated double bond is used.

For suitable examples of the monomer, there can be mentioned monovinyl aromatic monomers, acrylic

monomers, vinyl ester monomers, vinyl ether monomers, diolefin monomers and monoolefin monomers.

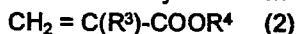
As the monovinyl aromatic monomer, there can be mentioned monomers represented by the following formula :



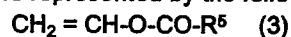
5 wherein Bz represents a benzene nucleus, R^1 represents a hydrogen atom, a lower alkyl group or a halogen atom, and R^2 represents a hydrogen atom, a lower alkyl group, a halogen atom, an alkoxy group, an amino group, a nitro group, a vinyl group or a carboxyl group.

For example, at least one monovinyl aromatic hydrocarbon selected from the group consisting of styrene, α -methylstyrene, vinyltoluene, α -chlorostyrene, o-chlorostyrene, m-chlorostyrene, p-chlorostyrene, p-ethylstyrene, sodium styrene-sulfonate and divinylbenzene is used.

As the other monomer, there can be mentioned acrylic monomers represented by the following formula :

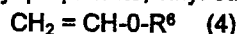


15 wherein R^3 represents a hydrogen atom or a lower alkyl group, and R^4 represents a hydrogen atom, a hydrocarbon group having up to 12 carbon atoms, a hydroxyalkyl group, a vinyl ester group or an aminoalkyl group, such as acrylic acid, methacrylic acid, methyl acrylate, ethyl acrylate, butyl acrylate, 2-ethylhexyl acrylate, cyclohexyl acrylate, phenyl acrylate, methyl methacrylate, hexyl methacrylate, 2-ethylhexyl methacrylate, ethyl 3-hydroxyacrylate, propyl γ -hydroxyacrylate, butyl δ -hydroxyacrylate, ethyl β -hydroxymethacrylate, propyl γ -aminoacrylate, propyl γ -N,N-diethylaminoacrylate, ethylene glycol dimethacrylic acid ester and tetraethylene glycol dimethacrylic acid ester, vinyl esters represented by the following formula :

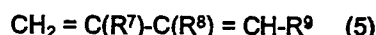


20 wherein R^5 represents a hydrogen atom or a lower alkyl group,

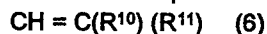
such as vinyl formate, vinyl acetate and vinyl propionate, vinyl ethers represented by the following formula :



25 wherein R^6 represents a monovalent hydrocarbon group having up to 12 carbon atoms, such as vinylmethyl ether, vinylethyl ether, vinyl-n-butyl ether, vinylphenyl ether and vinylcyclohexyl ether, diolefins represented by the following formula :



wherein R^7 , R^8 and R^9 each represent a hydrogen atom, a lower alkyl group or a halogen atom, such as butadiene, isoprene and chloroprene, and monoolefins represented by the following formula :



30 wherein R^{10} and R^{11} each represent a hydrogen atom or a lower alkyl group,

such as ethylene, propylene, isobutylene, butene-1, pentene-1 and 4-methylpentene-1.

(b) Polymerization initiator

35 In the suspension polymerization of the present invention, a polymerization initiator is used, and as the polymerization initiator, there can be mentioned radical-polymerizable initiators, for example, azo compounds such as 2,2-azobis(2,4-methoxy-2,4-dimethylvalero-nitrile and 2,2-azobis(2-cyclopropylpropionitrile, and peroxides such as cumene hydroperoxide, t-butyl hydroperoxide, dicumyl peroxide, di-t-butyl peroxide, benzoyl peroxide and lauroyl peroxide. Furthermore, ionizing radiations such as γ -rays and accelerated electron beams, and various sensitizers can be used in combination with the polymerization initiator.

The amount added of the polymerization initiator such as an azo compound or peroxide is preferred to be used in an amount of 0.1 to 20% by weight based on the charged monomer.

45 At least one polymerization initiator having a half-value period of up to 30 minutes is used at the suspension polymerization. The half-value period of up to 30 minutes is the value determined under the reaction temperature conditions adopted for the suspension polymerization, and in the case where a polymerization promoter is used, the half-value period in the state influenced by the polymerization promoter is meant.

(c) Crosslinking agent

50 A crosslinking agent is added at the suspension polymerization to promote the polymerization of the vinyl monomer and the increase of the bulky polymer.

Any of known crosslinking agents, for example, divinyl compounds such as divinylbenzene, divinyl ether and divinyl sulfone, diallyl compounds such as allyl phthalate and diallylcarbinol, diacryl esters such as diacrylphenol, and ethylene glycol dimethacrylate, trimethylol propane triacrylate, glycidyl methacrylate and glycidyl acrylate, can be used. A diacryl ester especially preferably used.

(d) Other additives used at polymerization step

In the present invention, a polymerization promoter, a crosslinking agent and a chain transfer agent can be used according to need. Known additives can be added in appropriate amounts.

Furthermore, in order to perform granulation or the like smoothly, a known surface active agent or dispersant can be added at the polymerization step.

5

(e) Coloring agent

Known dyes and pigments can be used as the coloring agent. Specific examples are described below.

10

a. Black pigment

Carbon black, acetylene black, lamp black and aniline black.

b. Yellow pigment

15

Chrome yellow, cadmium yellow, yellow iron oxide, Mineral Fast Yellow, nickel titanium yellow, Naples Naphthol Yellow S, Hansa Yellow 10G, Benzidine Yellow G, Quinoline Yellow Lake, Permanent Yellow NGG and Tartrazine Lake.

20

c. Orange pigment

Chrome orange, molybdenum orange, Permanent Orange GTR, Pyrazolone Orange, Vulcan Orange, Indanthrene Brilliant Orange EK, Benzidine Orange G and Indanthrene Brilliant Orange GR.

25

d. Red pigment

Red iron oxide, cadmium red, red lead, mercury cadmium sulfide, Permanent Orange 4R, Lithol Red, Pyrazolone Red, Watchung Red calcium salt, Lake Red D, Brilliant Carmine 6B, Eosine Lake, Rhodamine Lake B, Alizarine Lake and Brilliant Carmine 3B.

30

e. Violet pigment

Manganese violet, Fast Violet B and Methyl Violet Lake.

35

f. Blue pigment

Iron blue, cobalt blue, Alkali Blue Lake, Victoria Blue Lake, Phthalocyanine Blue, metal-free Phthalocyanine Blue, partially chlorinated Phthalocyanine Blue, Fast Sky Blue and Indanthrene Blue BC.

40

g. Green pigment

Chrome green, chromium oxide, Pigment Green B, Marachite Green Lake and Fast Yellow Green G.

h. White pigment

45

Zinc flower, titanium oxide, antimony white and zinc sulfide.

i. Extender pigment

50

Baryte powder, barium carbonate, clay, silica, white carbon, talc and aluminum white.

The coloring pigment can be added in an amount of 1 to 20 parts by weight, preferably 5 to 15 parts by weight, per 100 parts by weight of the polymerizable monomer.

(f) Other additives to be incorporated into toner

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Releasing agents such as low-molecular-weight polyethylene, low-molecular-weight polypropylene, various waxes and silicone oils can be incorporated into the toner so as to impart an offset-preventing effect to the toner. The releasing agent can be added in an amount of 0.1 to 10 parts by weight, preferably 0.5 to 8 parts

by weight, per 100 parts by weight of the polymerizable monomer.

As the magnetic pigment, there are known triiron tetroxide (Fe_3O_4), diiron trioxide ($\gamma\text{-Fe}_2\text{O}_3$), zinc ironoxide (ZnFe_2O_4), yttrium iron oxide ($\text{Y}_3\text{Fe}_5\text{O}_{12}$), cadmium iron oxide ($\text{Gd}_3\text{Fe}_5\text{O}_{12}$), copper iron oxide (CuFe_2O_4), lead iron oxide ($\text{PbFe}_{12}\text{O}_{19}$), neodymium iron oxide (NdFeO_3), barium iron oxide ($\text{BaFe}_{12}\text{O}_{19}$), magnesium iron oxide (5) (MgFe_2O_4), manganese iron oxide (MnFe_2O_4), lanthanum iron oxide (LaFeO_3), iron powder (Fe), cobalt powder (Co) and nickel powder (Ni). In the present invention, any of fine powders of these known magnetic materials can be optionally used.

Known charge-controlling agents such as a metal-containing azo dye, a metal compound of (alkyl)salicylic acid, a metal soap of naphthenic acid, a metal soap of a fatty acid and a soap of a resin acid can be added to 10 adjust the chargeability of the toner. The charge-controlling agent can be used in an amount of 0.1 to 10 parts by weight, preferably 0.5 to 5 parts by weight, per 100 parts by weight of the polymerizable monomer.

The polymerizable monomer and additives represented by the coloring agent are sufficiently mixed and dispersed and then subjected to the suspension polymerization.

15 Suspension Polymerization

In the suspension polymerization, a water-soluble dispersion medium is ordinarily used. For example, water and alcohols are used. The vinyl monomer is generally suspended in an amount of 100 to 2,000 g in 1 liter of the dispersion medium, though the amount of the monomer is changed to some extent according to the kind 20 thereof. A surface active agent or a dispersion stabilizer is used for suspension granulation. Known surface active agents and dispersion stabilizers can be used, and an anionic surface active agent of the fatty acid or sulfonic acid type is preferably used as the surface active agent and a hardly soluble inorganic salt is preferably used as the dispersion stabilizer.

The suspension granulation in the dispersion medium is accomplished by a high-speed shearing stirrer 25 such as a homomixer or a homogenizer, and it is preferred that the size of granulated particles be 3 to 20 μm . If the size of the granulated particles is adjusted within this range, toner particles having an appropriate particle size can be obtained.

At the suspension polymerization, at least one initiator having a half-value period of up to 30 minutes, especially up to 20 minutes, optionally together with a gentle polymerization initiator, and a crosslinking agent are 30 added, as pointed out hereinafter. The addition can be appropriately performed before or after the granulation.

It is preferred that the reaction be carried out at a temperature of 30 to 100°C, especially 40 to 90°C. Furthermore, in the present invention, it is preferred that the reaction temperature be changed and dropped in the midway. More specifically, it is preferred that within 10 to 60 minutes after the deactivation of the polymerization 35 initiator having a short half-value period, the reaction temperature be dropped by 5 to 30°C. If the reaction temperature is thus dropped, the remaining polymerization initiator effects gentle reaction, and a high-molecular-weight polymer and a low-molecular-weight polymer can be easily formed. Incidentally, the half-value period is the value determined at the above temperature in the suspension polymerization reaction system.

A releasing agent can be incorporated in the toner polymer of the present invention. The releasing agent 40 can be added to the vinyl monomer or after the polymerization. However, it is preferred that the releasing agent be added to the monomer. The releasing agent in the toner exerts the function of preventing contamination of the fixing means, increasing the life of the fixing means and increasing the ratio of the low-molecular-weight polymer.

Toner Particles

45 The obtained toner particles comprise low-molecular-weight and high-molecular-weight polymers, and both the polymers have an antiblocking property and additives such as the coloring agent are included in the polymer chains.

In the molecular weight distribution, the minimum molecular weight peak is at a position of a molecular 50 weight lower than 50,000, preferably 3,000 to 50,000, especially preferably 5,000 to 40,000, and the maximum molecular weight peak is at a position of a molecular weight higher than 200,000, preferably 200,000 to 7,000,000, especially preferably 300,000 to 5,000,000. Apparently, the low-molecular-weight polymer and the high-molecular-weight polymer are present in the toner. If the position of the maximum molecular weight peak is a position of a molecular weight lower than 200,000, it becomes difficult to impart sufficient offset resistance, 55 antiblocking property and wear resistance. If the position of the minimum molecular weight peak is a position of a molecular weight higher than 50,000, it becomes difficult to impart a sufficient fixing property.

In the toner particles satisfying the above-mentioned requirement of the peak positions, the maximum molecular weight component, that is, the high-molecular-weight component having a molecular weight higher

than the molecular weight of the maximum peak, can be made present in an amount of 10 to 40%. The toner particles satisfying this requirement have improved blocking resistance and durability and excellent performances can be attained stably for a long time. If the content of the maximum molecular weight component is outside the above-mentioned range and becomes too low, the long-time stability is degraded and contamination of the fixing means or roller is often caused. If the content of the maximum molecular weight component is too high, the fixing property is often degraded.

The toner particles obtained by the suspension polymerization have a spherical shape, and moreover, the coloring agent, the releasing agent and the like are included in the polymer chains and the separation of the additives can be prevented, with the result that the durability and flowability are improved.

The toner particles have the following viscosity characteristics in addition to the above-mentioned structural characteristics. When the viscosity of the toner is measured by a flow tester, in the temperature range of from 100 to 150°C, at which the toner is heated at the fixing step, the temperature difference required for the viscosity of the toner to change from 5×10^6 poise to 5×10^4 poise can be at least 32°C, preferably at least 35°C. In the toner where this temperature difference is maintained, the change of the viscosity is small, and the toner has excellent fixing property, offset resistance and apparatus adaptability.

In the toner of the present invention, it is preferred that the viscosity gradient (absolute value) in the above-mentioned temperature range be in the range of from 0.02 to 0.07/°C and there be present at least one region where the viscosity gradient (absolute value) is smaller than 0.03/°C, especially smaller than 0.026/°C. Furthermore, it is preferred that there be present at least two regions where the viscosity gradient is smaller than 0.03/°C, a first region be present in a temperature range of from 115 to 125°C and the other region be present in a temperature range of from 130 to 140°C. For example, Fig. 1 is a characteristic curve illustrating the relation between the temperature and the viscosity in the toner of the present invention. In Fig. 1, the temperature is plotted on the abscissa and the logarithm of the viscosity is plotted on the ordinate. As is seen from the viscosity change curve A of the toner of the present invention, 40°C is necessary for the viscosity to change from 5×10^6 poise to 5×10^4 poise, and the gradient is considerably gentle as compared with the gradient of the curve B of the conventional toner where only less than 30°C is necessary for this change of the viscosity. In the toner of the present invention, the viscosity gradient is -0.014/°C in the temperature range of from 115 to 125°C and is -0.025/°C in the temperature range of from 130 to 140°C.

In connection with the viscosity characteristics of the toner, it is further preferred that in the above-mentioned temperature range, the proportion of the region where the viscosity gradient is lower than the average viscosity gradient (absolute value) of the toner be at least 10%, especially at least 15%. Moreover, in the polymerized resin, preferably, the requirements of $(T_i - T_g) \leq 50$ and $(T_m - T_i) \geq 30$ are satisfied among the glass transition temperature T_g , the flow-out initiating temperature T_i of the toner and the temperature T_m of flow-out of 1/2 of the toner.

The present invention will now be described in detail with reference to the following examples that by no means limit the scope of the invention.

Example 1

A mixture comprising 80 parts by weight of styrene, 20 parts by weight of 2-ethylhexyl methacrylate, 5 parts by weight of carbon black (MA-100 supplied by Mitsubishi Kasei), 1 part by weight of a charge-controlling agent (Bontron S-40 supplied by Orient Kagaku), 1 part by weight of divinylbenzene and 7 parts by weight of 2,2'-azobis(2,4-dimethylvaleronitrile) (the half-value period at 80°C is about 10 minutes) as the polymerization initiator was added into a continuous phase comprising 400 parts by weight of water, 6 parts by weight of tricalcium phosphate and 0.01 part by weight of sodium dodecylbenzenesulfonate, and the mixture was granulated by using a homomixer. The temperature was elevated to 80°C and polymerization was carried out for 10 hours. The obtained polymer was treated with a dilute acid, washed with water and dried to obtain toner particles. When the particle size characteristics were determined by using a Coulter counter, it was found that the median diameter D_{50} based on the volume was 10.3 μm and the toner particles had a sharp particle size distribution.

When the molecular weight distribution was measured by GPC, it was found that as shown in Fig. 2, there were present two peaks, the weight average molecular weight (Mw) of the entire particles was 340,000, the high-molecular-weight peak was present at a position of a molecular weight of 1,200,000 and the low-molecular-weight peak was present at a position of a molecular weight of 35,000.

Hydrophobic silica was added in an amount of 0.1 part by weight per 100 parts by weight of the obtained toner, and then, the toner was mixed with a carrier comprising ferrite particles coated with a silicone resin so that the toner concentration was 3%, whereby a developer was prepared. The obtained developer was subjected to the printing test for obtaining 10,000 prints at a copying speed of 12 A-4 sheets per minute (transverse feed) in an electrophotographic copying machine (Model DC-1205 supplied by Mita Industrial Co., Ltd.), and

the fixing property and offset resistance were evaluated. Incidentally, the fixing property was examined in the following manner. Namely, a transfer sheet having a toner image formed thereon was passed through fixing means to fix the toner image, an adhesive tape was press-bonded to the obtained fixed image and the adhesive tape was peeled. The density of the fixed image was measured before and after the peeling by a reflection densitometer (supplied by Tokyo Denshoku), and the fixing ratio was calculated according to the following formula and the fixing property was evaluated based on this fixing ratio :

$$\text{Fixing ratio (\%)} = \frac{\text{image density after peeling}}{\text{image density before peeling}} \times 100$$

The offset resistance was evaluated based on whether or not the offset phenomenon took place during the continuous copying operation. Furthermore, the wear resistance was evaluated based on the state of formation of fine particles. The antiblocking property was evaluated in the following manner. Namely, 20 g of the toner was charged in a glass cylinder having an inner diameter of 26.5 mm in an oven maintained at a temperature of 60°C, and a weight of 100 g was placed on the toner and the toner was allowed to stand still in this state for 30 minutes. Then, the cylinder was removed and the antiblocking property was evaluated whether or not the toner collapsed.

The obtained results are shown in Table 1.

In Table 1, in the column of the fixing property, ○ indicates a fixing ratio of at least 95%, n indicates a fixing ratio of at least 90%, and X indicates a fixing ratio lower than 90%.

In the column of the antiblocking property, ○ indicates that the toner collapsed on removal of the cylinder, △ indicates that the toner collapsed by pressing the toner by the finger, and X indicates that the toner did not collapse.

In the column of the wear resistance, ○ indicates that fine particles were not formed in the developing machine, △ indicates that slight formation of the fine particles in the developing machine was observed, and X indicates that formation of fine particles in the developing machine was conspicuous.

Example 2

In the same manner as described in Example 1, a mixture comprising 80 parts by weight of styrene, 20 parts by weight of n-butyl methacrylate ; 5 parts by weight of carbon black (MA-100 supplied by Mitsubishi Kasei), 1 part by weight of a charge-controlling agent (Bontron S-40 supplied by Orient Kagaku), 1.1 parts by weight of divinylbenzene, 1.5 parts by weight of 2-ethylene glycol dimethacrylate and 7 parts by weight of 2,2'-azobis(2-cyclopropylpropionitrile) (the half-value period at 75°C is 11 minutes) as the polymerization initiator was added into the continuous phase and granulated. Then, suspension polymerization was carried out at 75°C for 6 hours to obtain toner particles.

The particle size characteristics of the obtained toner were such that the median diameter D₅₀ based on the volume was 10.2 μm and the particle size distribution was sharp. When the molecular weight distribution was measured by GPC, it was found that peaks were present at positions of molecular weights of 1,600,000 and 30,000 and the weight average molecular weight of the entire toner was 510,000.

In the same manner as described in Example 1, a developer was prepared by using the obtained toner and was tested. The obtained results are shown in Table 1.

Example 3

In the same manner as described in Example 1, a mixture comprising 80 parts by weight of styrene, 20 parts by weight of n-butyl methacrylate, 5 parts by weight of carbon black (#-100 supplied by Mitsubishi Kasei), 1 part by weight of a charge-controlling agent (Bontron S-40 supplied by Orient Kagaku), 1.0 part by weight of divinylbenzene, 1.5 parts by weight of 2-ethylene glycol dimethacrylate and 7 parts by weight of 2,2'-azobis(4-methoxy-2,4-dimethylvaleronitrile) (the half-value period at 60°C is about 12 minutes) as the polymerization initiator was added into the continuous phase and granulated. Then, suspension polymerization was carried out at 60°C for 11 hours to obtain a toner.

The particle size characteristics of the obtained toner were such that the median diameter D₅₀ based on

the volume was 11.0 μm and the particle size distribution was sharp. When the molecular weight distribution was measured by GPC, it was found that peaks were present at positions of molecular weights of 1,300,000 and 28,000 and the weight average molecular weight of the entire toner was 430,000.

In the same manner as described in Example 1, a developer was prepared by using the obtained toner and was tested.

The obtained results are shown in Table 1.

Example 4

In the same manner as described in Example 1, a mixture comprising 80 parts by weight of styrene, 20 parts by weight of n-butyl methacrylate, 5 parts by weight of carbon black (MA-100 supplied by Mitsubishi Kasei), 1 part by weight of a charge-controlling agent (Bontron S-40 supplied by Orient Kagaku), 1.8 parts by weight of divinylbenzene, 1.5 parts by weight of 2-ethylene glycol dimethacrylate and 10 parts by weight of 2,2'-azobis(2,4-dimethylvaleronitrile) (the half-value period at 80°C is about 10 minutes) as the polymerization initiator was added into the continuous phase and granulated. Then, suspension polymerization was carried out at 80°C for 9 hours to obtain toner particles.

The particle size characteristics of the obtained toner were such that the median diameter D_{50} based on the volume was 9.5 μm and the particle size distribution was sharp. When the molecular weight distribution was measured by GPC, it was found that peaks were present at positions of molecular weights of 7,900,000 and 5,600 and the weight average molecular weight of the entire toner was 2,500,000.

In the same manner as described in Example 1, a developer was prepared by using the obtained toner and was tested. The obtained results are shown in Table 1.

Comparative Example 1

A toner was prepared by carrying out the suspension polymerization for 13 hours in the same manner as described in Example 1 except that the polymerization temperature was changed to 65°C (the half-value period of 2,2'-azobis(2,4-dimethylvaleronitrile) as the initiator at 65°C is 100 minutes).

The particle size characteristics of the obtained toner were such that the median diameter D_{50} based on the volume was 10.4 μm and the particle size distribution was sharp. When the molecular weight distribution was measured by GPC, it was found that peaks were present at positions of molecular weights of 4,000,000 and 100,000 and the weight average molecular weight of the entire toner was 1,000,000.

In the same manner as described in Example 1, a developer was prepared by using the obtained toner and was tested. The obtained results are shown in Table 1.

Comparative Example 2

A toner was prepared by carrying out the polymerization reaction in the same manner as described in Example 1 except that divinylbenzene as the crosslinking agent was not used.

The particle size characteristics of the obtained toner were such that the median diameter D_{50} based on the volume was 10.1 μm and the particle size distribution was sharp. When the molecular weight distribution was measured by GPC, it was found that only a single peak was present and the weight average molecular weight of the entire toner was 1,000,000.

In the same manner as described in Example 1, a developer was prepared by using the obtained toner and was tested. The obtained results are shown in Table 1.

Comparative Example 3

A toner was prepared by carrying out the polymerization reaction in the same manner as described in Example 1 except that the polymerization temperature was changed to 60°C (the half-value period of 2,2'-azobis(2-cyclopropylpropionitrile) at 60°C is 65 minutes).

The particle size characteristics of the obtained toner were such that the median diameter of D_{50} based on the volume was 9.8 μm and the particle size distribution was sharp. When the molecular weight distribution was measured by GPC, it was found that peaks were present at positions of molecular weights of 1,800,000 and 850,000 and the weight average molecular weight of the entire toner was 1,100,000.

In the same manner as described in Example 1, a developer was prepared by using the obtained toner and was tested. The obtained results are shown in Table 1.

Table 1

	Median Diameter (μm) Based on Volume	Molecular Weight Characteristics		Fixing Property	Offset Resis- tance	Anti- blocking Property	Wear Resistance
		maximum peak position	minimum peak position				
<u>Example 1</u>	10.3	1,200,000	35,000	○	○	○	△
<u>Example 2</u>	10.2	1,600,000	30,000	○	○	○	○
<u>Example 3</u>	11.0	1,300,000	28,000	○	○	○	○
<u>Example 4</u>	9.5	7,900,000	5,600	△	○	○	○
<u>Comparative Example 1</u>	10.4	4,000,000	100,000	x	○	○	○
<u>Comparative Example 2</u>	10.1	—	—	○	x	x	x
<u>Comparative Example 3</u>	9.8	1,800,000	850,000	x	○	○	○

Example 5

In the same manner as described in Example 1, a mixture comprising 80 parts by weight of styrene, 20 parts by weight of 2-ethylhexyl methacrylate, 5 parts by weight of carbon black (MA-100 supplied by Mitsubishi Kasei), 1 part by weight of a charge-controlling agent (Bontron S-40 supplied by Orient Kagaku), 1.8 parts by weight of divinylbenzene, 1.5 parts by weight of 2-ethylene glycol dimethacrylate, 2 parts by weight of low-molecular-weight polypropylene (Biscol 550P supplied by Sanyo Kasei) and 10 parts by weight of 2,2'-azobis(2,4-dimethylvaleronitrile) (the half-value period at 80°C is about 10 minutes) as the polymerization initiator was added into the continuous phase and granulated. Then, suspension polymerization was carried out at 80°C for 10 hours to obtain toner particles.

The particle size characteristics of the obtained toner were such that the median diameter D_{50} based on the volume was 11.2 μm and the particle size distribution was sharp. When the molecular weight distribution was measured by GPC, it was found that a plurality of peaks were present, as shown in Fig. 3, and the weight average molecular weight (M_w) of the entire toner was 1,900,000, the maximum molecular weight peak was located at a position of a molecular weight of 6,100,000 and the minimum molecular weight peak was located at a position of a molecular weight of 44,000. Then, hydrophobic silica was added in an amount of 0.1 part by weight per 100 parts by weight of the obtained toner, and the toner was mixed with a carrier comprising ferrite particles coated with a silicone resin so that the toner concentration was 3%, whereby a developer was prepared. The obtained developer was subjected to the copying test for obtaining 20,000 prints in an electrophotographic copying machine (Model DC-1205 supplied by Mita Industrial Co., Ltd.), and the fixing property and offset resistance were evaluated.

The obtained results are shown in Table 2.

Example 6

In the same manner as described in Example 5, a mixture comprising 80 parts by weight of styrene, 20 parts by weight of n-butyl methacrylate, 5 parts by weight of carbon black (#-1000 supplied by Mitsubishi Kasei), 1 part by weight of a charge-controlling agent (Bontron S-40 supplied by Orient Kagaku), 1.3 parts by weight of divinylbenzene, 2 parts by weight of low-molecular-weight polypropylene (Biscol 660P supplied by Sanyo Kasei) and 7 parts by weight of 2,2'-azobis(2,4-dimethylvaleronitrile) (the half-value period at 80°C is about 10 minutes) as the polymerization initiator was added into the continuous phase and granulated. Then, suspension polymerization was carried out at 80°C for 10 hours to obtain toner particles.

The particle size characteristics of the obtained toner were such that the median diameter D_{50} based on the volume was 9.5 μm and the particle size distribution was sharp. When the molecular weight distribution was measured by GPC, it was found that maximum and minimum molecular weight peaks were present at positions of molecular weights of 2,100,000 and 38,000 and the weight average molecular weight of the entire toner was 640,000.

In the same manner as described in Example 5, a developer was prepared by using the obtained toner and was tested. The obtained results are shown in Table 2.

Example 7

In the same manner as described in Example 5, a mixture comprising 75 parts by weight of styrene, 25 parts by weight of 2-ethylhexyl methacrylate, 5 parts by weight of carbon black (#-1000 supplied by Mitsubishi Kasei), 1 part by weight of a charge-controlling agent (Bontron S-40 supplied by Orient Kagaku), 1.0 parts by weight of divinylbenzene, 2 parts by weight of low-molecular-weight polypropylene (Biscol 550P supplied by Sanyo Kasei) and 5 parts by weight of 2,2'-azobis(4-methoxy-2,4-dimethylvaleronitrile) (the half-value period at 80°C is about 10 minutes) as the polymerization initiator was added into the continuous phase and granulated. Then, suspension polymerization was carried out at 80°C for 10 hours to obtain toner particles.

The particle size characteristics of the obtained toner were such that the median diameter D_{50} based on the volume was 10.3 μm and the particle size distribution was sharp. When the molecular weight distribution was measured by GPC, it was found that maximum and minimum molecular weight peaks were present at positions of molecular weights of 1,100,000 and 28,000 and the weight average molecular weight of the entire toner was 300,000.

In the same manner as described in Example 5, a developer was prepared by using the obtained toner and was tested. The obtained results are shown in Table 2.

Comparative Example 4

A toner was prepared by carrying out the suspension polymerization for 11 hours in the same manner as described in Example 5 except that the polymerization temperature was changed to 65°C (the half-value period of 2,2'-azobis(4-methoxy-2,4-dimethylvaleronitrile) as the initiator at 65°C is 100 minutes).

5 The particle size characteristics of the obtained toner were such that the median diameter D_{50} based on the volume was 11.0 μm and the particle size distribution was sharp. When the molecular weight distribution was measured by GPC, it was found that maximum and minimum molecular weight peaks were present at positions of molecular weights of 12,000,000 and 800,000 and the weight average molecular weight of the entire toner was 4,000,000.

10 In the same manner as described in Example 5, a developer was prepared by using the obtained toner and was tested. The obtained results are shown in Table 2.

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Table 2

	<u>Particle Size Characteristics</u>		<u>Molecular Weight Characteristics</u>		<u>Fixing Property</u>	<u>Offset Resistance</u>	<u>Anti-blocking Property</u>	<u>Wear Resistance</u>	<u>Contamination of Roller</u>
	median diameter (μm) based on volume	molecular weight of maximum peak	molecular weight of minimum peak						
<u>Example 5</u>	11.2	6,100,000	44,000		○	○	○	○	○
<u>Example 6</u>	9.5	2,100,000	38,000		○	○	○	○	○
<u>Example 7</u>	10.3	1,100,000	28,000		○	○	△	○	○
<u>Comparative Example 4</u>	11.0	12,000,000	800,000	x		○	○	○	○

Example 8

A mixture comprising 80 parts by weight of styrene, 20 parts by weight of 2-ethylhexyl methacrylate, 5 parts by weight of carbon black (MA-100 supplied by Mitsubishi Kasei), 1 part by weight of a charge-controlling agent (Bontron S-40 supplied by Orient Kagaku), 0.7 part by weight of divinylbenzene 1.5 parts by weight of 2-ethylene glycol dimethacrylate, 4 parts by weight of 2,2'-azobis(4-methoxy-2,4-dimethylvaleronitrile) (the half-value period at 70°C is 3.5 minutes and the half-value period at 60°C is about 12 minutes) as the polymerization initiator and 2 parts by weight of 2,2'-azobis(2,4-dimethylvaleronitrile) (the half-value period at 70°C is about 40 minutes and the half-value period at 60°C is about 180 minutes) as the polymerization initiator was added into a continuous phase comprising 400 parts by weight of water, 6 parts by weight of tricalcium phosphate and 0.01 part by weight of sodium dodecylbenzenesulfonate, and the mixture was granulated by using a homomixer. The temperature was elevated to 70°C and polymerization was carried out for 30 minutes, and polymerization was further conducted at 60°C for 8 hours. The obtained polymer was treated with a dilute acid, washed with water and dried to obtain toner particles. When the particle size characteristics were determined by using a Coulter counter, it was found that the median diameter D_{50} based on the volume was 10.7 μm and the toner particles had a sharp particle size distribution.

When the molecular weight distribution was measured by GPC, it was found that as shown in Fig. 4, there were present two peaks, the weight average molecular weight (M_w) of the entire particles was 410,000, the high-molecular-weight peak was present at a position of a molecular weight of 2,300,000 and the low-molecular-weight peak was present at a position of a molecular weight of 29,000. The proportion of the high-molecular-weight component (hatched portion in Fig. 4) having a molecular weight higher than the maximum molecular weight peak was 15.6% based on the entire polymer. The viscosity change gradient curve of the obtained toner particles was a gentle monotonous decrease curve as shown in Fig. 1. The gradient at temperatures of from 120 to 125°C was -0.014/°C and the gradient at temperatures of from 135 to 140°C was -0.025/°C.

Hydrophobic silica was added in an amount of 0.1 part by weight per 100 parts by weight of the obtained toner, and then, the toner was mixed with a carrier comprising ferrite particles coated with a silicone resin so that the toner concentration was 3%, whereby a developer was prepared. The obtained developer was subjected to the printing test for obtaining 20,000 prints in an electrophotographic copying machine (Model DC-1205 supplied by Mita Industrial Co., Ltd.), and the fixing property and offset resistance were evaluated.

The obtained results are shown in Table 3.

Example 9

In the same manner as described in Example 8, a mixture comprising 70 parts by weight of styrene, 30 parts by weight of 2-ethylhexyl methacrylate, 5 parts by weight of carbon black (#-1000 supplied by Mitsubishi Kasei), 1 part by weight of a charge-controlling agent (Bontron S-40 supplied by Orient Kagaku), 0.9 part by weight of divinylbenzene, 4 parts by weight of 2,2'-azobis(2,4-dimethylvaleronitrile) (the half-value period at 85°C is about 5 minutes and the half-value period at 75°C is about 30 minutes) as the polymerization initiator and 2 parts by weight of 2,2'-azobis(2-methylpropionitrile)(2,2'-azobisisobutyronitrile) (the half-value period at 85°C is about 50 minutes and the half-value period at 75°C is about 200 minutes) as the polymerization initiator was added into the continuous phase and granulated. Then, suspension polymerization was carried out at 85°C for 40 minutes and at 75°C for 8 hours to obtain toner particles.

The particle size characteristics of the obtained toner were such that the median diameter D_{50} based on the volume was 9.6 μm and the particle size distribution was sharp. When the molecular weight distribution was measured by GPC, it was found that maximum and minimum molecular weight peaks were present at positions of molecular weights of 3,200,000 and 15,000 and the weight average molecular weight of the entire toner was 860,000. The proportion of the high-molecular weight component having a molecular weight exceeding the maximum peak was 29%.

In the same manner as described in Example 8, a developer was prepared by using the obtained toner and was tested. The obtained results are shown in Table 3.

Example 10

In the same manner as described in Example 8, a mixture comprising 70 parts by weight of styrene, 30 parts by weight of n-butyl methacrylate, 5 parts by weight of carbon black (#-1000 supplied by Mitsubishi Kasei), 1 part by weight of a charge-controlling agent (Bontron S-40 supplied by Orient Kagaku), 1.0 part by weight of divinylbenzene, 2 parts by weight of 2,2'-azobis(2-methylpropionitrile)(2,2'-azobisisobutyronitrile) (the half-value period at 80°C is about 100 minutes and the half-value period at 75°C is about 200 minutes) as the polym-

erization initiator and 4 parts by weight of 2,2'-azobis(2-cyclopropylpropionitrile) (the half-value period at 80°C is 6.5 minutes and the half-value period at 75°C is about 12 minutes) as the polymerization initiator was added into the continuous phase and granulated. Then, suspension polymerization was carried out at 80°C for 40 minutes and at 75°C for 8 hours to obtain toner particles.

5 The particle size characteristics of the obtained toner were such that the median diameter D_{50} based on the volume was 10.4 μm and the particle size distribution was sharp. When the molecular weight distribution was measured by GPC, it was found that maximum and minimum molecular weight peaks were present at positions of molecular weights of 3,800,000 and 20,000 and the weight average molecular weight of the entire toner was 950,000. The proportion of the high-molecular-weight component exceeding the maximum peak was 32%.

10 In the same manner as described in Example 8, a developer was prepared by using the obtained toner and was tested. The obtained results are shown in Table 3.

Example 11

15 In the same manner as described in Example 8, a mixture comprising 70 parts by weight of styrene, 30 parts by weight of n-butyl methacrylate, 5 parts by weight of carbon black (MA-100 supplied by Mitsubishi Kasei), 1 part by weight of a charge-controlling agent (Bontrol S-40 supplied by Orient Kagaku), 0.9 part by weight of divinylbenzene, 1.5 parts by weight of 2-ethylene glycol dimethacrylate, 4 parts by weight of 2,2'-azobis(2-cyclopropionitrile) (the half-value period at 80°C is 6.5 minutes) as the polymerization initiator and 2 parts
20 by weight of 2,2'-azobis(2-methylbutyronitrile) (the half-value period at 80°C is about 130 minutes) as the polymerization initiator was added into the continuous phase and granulated. Then, suspension polymerization was carried out at 80°C for 10 hours to obtain toner particles.

The particle size characteristics of the obtained toner were such that the median diameter D_{50} based on the volume was 9.4 μm and the particle size distribution was sharp. When the molecular weight distribution
25 was measured by GPC, it was found that maximum and minimum molecular weight peaks were present at positions of molecular weights of 1,800,000 and 19,000 and the weight average molecular weight of the entire toner was 550,000. The proportion of the high-molecular-weight component exceeding the maximum molecular weight peak was 25%.

In the same manner as described in Example 8, a developer was prepared by using the obtained toner
30 and was tested. The obtained results are shown in Table 3.

Comparative Example 5

A toner was prepared by carrying out the polymerization in the same manner as described in Example 8
35 except that 2,2'-azobis(2,4-dimethylvaleronitrile) as the polymerization initiator was changed to 2,2'-azobis(2-cyclopropylpropionitrile) and the initial polymerization temperature was changed to 50°C (the half-value period of 2,2'-azobis(2-cyclopropylpropionitrile) at 50°C is about 250 minutes and the half-value period of 2,2'-azobis(4-methoxy-2,4-dimethylvaleronitrile at 50°C is about 40 minutes).

The particle size characteristics of the obtained toner were such that the median diameter D_{50} based on the volume was 10.3 μm and the particle size distribution was sharp. When the molecular weight distribution
40 was measured by GPC, it was found that maximum and minimum molecular weight peaks were present at positions of molecular weights of 5,100,000 and 80,000 and the weight average molecular weight of the entire toner was 1,400,000. The proportion of the high-molecular-weight component exceeding the maximum molecular weight peak was 15%.

45 In the same manner as described in Example 8, a developer was prepared by using the obtained toner and was tested. The obtained results are shown in Table 3.

Comparative Example 6

50 A toner was prepared by carrying out the polymerization in the same manner as described in Example 9 except that the polymerization was conducted at a polymerization temperature of 70°C for 9 hours (the half-value period of 2,2'-azobis(2,4-dimethylvaleronitrile) at 70°C is about 40 minutes and the half-value period of 2,2'-azobis(2-methylpropionitrile) (2,2'-azobisisobutyronitrile) at 70°C is about 400 minutes).

The particle size characteristics of the obtained toner were such that the median diameter D_{50} based on the volume was 9.8 μm and the particle size distribution was sharp. When the molecular weight distribution
55 was measured by GPC, it was found that maximum and minimum molecular weight peaks were present at positions of molecular weights of 6,200,000 and 120,000 and the weight average molecular weight of the entire toner was 1,500,000. The proportion of the high-molecular-weight component exceeding the maximum molecu-

lar weight peak was 17%.

In the same manner as described in Example 8, a developer was prepared by using the obtained toner and was tested. The obtained results are shown in Table 3.

5 Comparative Example 7

A toner was prepared in the same manner as described in Example 9 except that divinylbenzene as the crosslinking agent was not used at all.

10 The particle size characteristics of the obtained toner were such that the median diameter D_{50} based on the volume was $9.9\ \mu\text{m}$ and the particle size distribution was sharp. When the molecular weight distribution was measured by GPC, it was found that maximum and minimum molecular weight peaks were present at positions of molecular weights of 1,200,000 and 120,000 and the weight average molecular weight of the entire toner was 860,000. The proportion of the high-molecular-weight component exceeding the maximum molecular weight peak was 43%.

15 In the same manner as described in Example 8, a developer was prepared by using the obtained toner and was tested. The obtained results are shown in Table 3.

Comparative Example 8

20 A mixture comprising 100 parts by weight of a styrene-acrylic copolymer, 7 parts by weight of carbon black (MA-100 supplied by Mitsubishi Kasei) and 0.5 part by weight of a charge-controlling agent (Bontron S-40 supplied by Orient Kagaku) was mold-kneaded on a roll mill at about 150°C . The kneaded composition was cooled, pulverized by an air jet mill and subjected to air classification to obtain a toner having a median diameter based on the volume of $11.3\ \mu\text{m}$. The viscosity change gradient curve of the obtained toner particles is a monotonous decrease curve as shown in B of Fig. 1. The viscosity gradient was larger than $0.030/^{\circ}\text{C}$ over the entire temperature range of from 115 to 145°C .

In the same manner as described in Example 8, a developer was prepared by using the obtained toner and the developer was tested. The obtained results are shown in Table 3.

30 Furthermore, the values T_g , T_i and T_m of the toners obtained in Examples 8, 9, 10 and 11 and Comparative Examples 6, 7 and 8 are shown in Table 4.

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Table 3

Particle Size Characteristics	Molecular Weight Characteristics				Fixing Property	Offset Resistance	Anti-blocking Property	Wear Resistance	Contamination of Roller
	molecular weight maximum	molecular weight minimum	molecular weight peak	Content(%) of high-molecular weight component exceeding maximum molecular weight peak					
median diameter (μm) based on volume									
<u>Example 8</u>	10.7	2,300,000	29,000	15.6	○	○	○	○	○
<u>Example 9</u>	9.6	3,200,000	15,000	29.0	○	○	○	○	○
<u>Example 10</u>	10.4	3,800,000	20,000	32.0	○	○	○	○	○
<u>Example 11</u>	9.4	1,800,000	19,000	25.0	○	○	○	△	△
<u>Comparative Example 5</u>	10.3	5,100,000	80,000	15.0	x	○	○	○	○
<u>Comparative Example 6</u>	9.8	6,200,000	120,000	17.0	x	○	○	○	○
<u>Comparative Example 7</u>	9.9	1,200,000	120,000	43.0	x	○	△	○	△
<u>Comparative Example 8</u>	11.3	—	—	—	x	x	△	—	x

Table 4

	<u>T_g (°C)</u>	<u>T_i (°C)</u>	<u>T_m (°C)</u>	
5				
	<u>Example 8</u>	66	107	150
10	<u>Example 9</u>	67	108	152
	<u>Example 10</u>	67	108	151
15	<u>Example 11</u>	65	106	148
	<u>Comparative Example 6</u>	70	122	151
20	<u>Comparative Example 7</u>	71	124	152
25	<u>Comparative Example 8</u>	65	117	146

30 From the results shown in Table 1, it is seen that a toner directly obtained by the suspension polymerization, which has a maximum molecular weight peak at a position of a molecular weight higher than 200,000 and a minimum molecular weight peak at a position of a molecular weight lower than 50,000, is excellent in all of fixing property, offset resistance, antiblocking property and wear resistance.

35 From the results shown in Table 2, it is seen that the toners of Examples 5, 6 and 7 satisfying the above-mentioned requirements of the molecular weight characteristics and containing low-molecular-weight polypropylene as the releasing agent exert an effect of effectively preventing contamination of a fixing roller while they have the above-mentioned characteristics as well as the toners of Examples 1, 2, 3 and 4.

40 In connection with the toners of Examples 8, 9, 10 and 11 and Comparative Examples 5, 6 and 7, the copying test for obtaining 20,000 prints was carried out at a copying speed of 32 A-4 sheets/minute (transverse feeding) in an electrophotographic copying machine (Model PC-3255). As is seen from the results shown in Table 3, the toners of Examples 8, 9, 10 and 11 were excellent in all of fixing property, offset resistance, antiblocking property and wear resistance and contamination the roller was not caused. In contrast, in the toners of Comparative Examples 5, 6 and 7, the fixing property was worsened and occurrence of the cold offset was observed. Furthermore, it was confirmed that the toners of Examples 8, 9, 10 and 11 showed a good adaptability to a copying machine in which a different copying speed was adopted and the fixing conditions were changed.

45 As is apparent from the foregoing description, the toner of the present invention consisting of spherical particles obtained by the suspension polymerization, which has a specific molecular weight distribution having a plurality of molecular weight peaks, is excellent in all of fixing property, antiblocking property and offset resistance. Furthermore, in the toner of the present invention, since specific viscosity characteristics of the toner particles are manifested in the temperature range of from 100 to 150°C at which the toner is heated at the fixing step, the fixing property and offset resistance are enhanced at the fixing step and the apparatus adaptability of the toner is improved.

55 Claims

1. A toner comprising spherical particles obtainable by suspension polymerization which comprise a binder resin and a coloring agent, wherein the median diameter of the particles based on the volume is in the range

of from 3 to 20 μ m, the molecular weight distribution of the particles has a plurality of peaks such that the peak of the minimum position in the molecular weight distribution is lower than 50,000 and the peak of the maximum position is higher than 200,000.

- 5 2. A toner according to claim 1, wherein the occupancy ratio of a high-molecular-weight component having a molecular weight higher than the maximum peak value is in the range of from 10 to 40% based on the entire particles.
- 10 3. A toner according to claim 1 or 2, wherein a releasing substance is incorporated in the suspension polymerization particles.
- 15 4. A toner according to any one of claims 1 to 3 wherein in the temperature range of from 100 to 150°C at which the toner is heated at the fixing step, the temperature difference required for the viscosity of the toner to change from 5×10^5 Pas to 5×10^3 Pas under heating is at least 32°C.
- 20 5. A toner according to any one of claims 1 to 4 wherein the flow characteristics of the binder resin of the toner are such that the flow-initiating temperature T_i satisfies the requirement of $(T_i - T_g) \leq 50$ in which T_g represents the glass transition temperature of the binder resin, and the temperature T_m for flow-out of half of the toner satisfies the requirement of $(T_m - T_i) \geq 30$.
- 25 6. A toner according to any one of claims 1 to 5 having an average viscosity gradient (absolute value), in the temperature range of from 100 to 150°C, of 0.02 to 0.7/°C, and in this temperature range having at least one region wherein the absolute value of the viscosity gradient is smaller than 0.03/°C.
- 30 7. A toner according to claim 6 having two regions where the absolute value of the viscosity gradient is smaller than 0.03/°C, these two regions being a region of from 115 to 125°C and a region of from 130 to 140°C.
- 35 8. A toner according to claim 6 or claim 7 wherein the region(s) where the viscosity gradient is gentler than the average viscosity gradient is at least 10% of the temperature range.
- 40 9. A process for the preparation of a toner by suspension polymerization using a vinyl monomer and a coloring agent, characterized in that an initiator having a half-value period of up to 30 minutes and a crosslinking agent are incorporated at the polymerization of said vinyl monomer and the polymerization is carried out so that the molecular weight distribution of the toner which is prepared has a plurality of peaks.
- 45 10. A process according to claim 9, wherein a releasing substance is incorporated in the polymerization.
- 50 11. A process for the preparation of a toner according to claim 9 or 10, wherein at least two initiators differing in their half-value periods are incorporated in the polymerization of the vinyl monomer, the half-value period of at least one of the initiators being up to 20 minutes.
- 55 12. A process for the preparation of a toner according to any one of claims 9 to 11, wherein the polymerization is carried out by incorporating at least one member selected from the group consisting of coloring agents, charge-controlling agents and magnetic materials.
13. A process for the preparation of a toner according to any one of claims 9 to 12, wherein the polymerization is carried out so that of a plurality of peaks of the molecular weight distribution, the minimum molecular weight peak is at a position lower than 50,000 and the maximum molecular weight peak is at a position higher than 200,000.
14. A process according to any one of claims 9 to 13 for producing a toner according to any one of claims 1 to 8.

FIG. 1

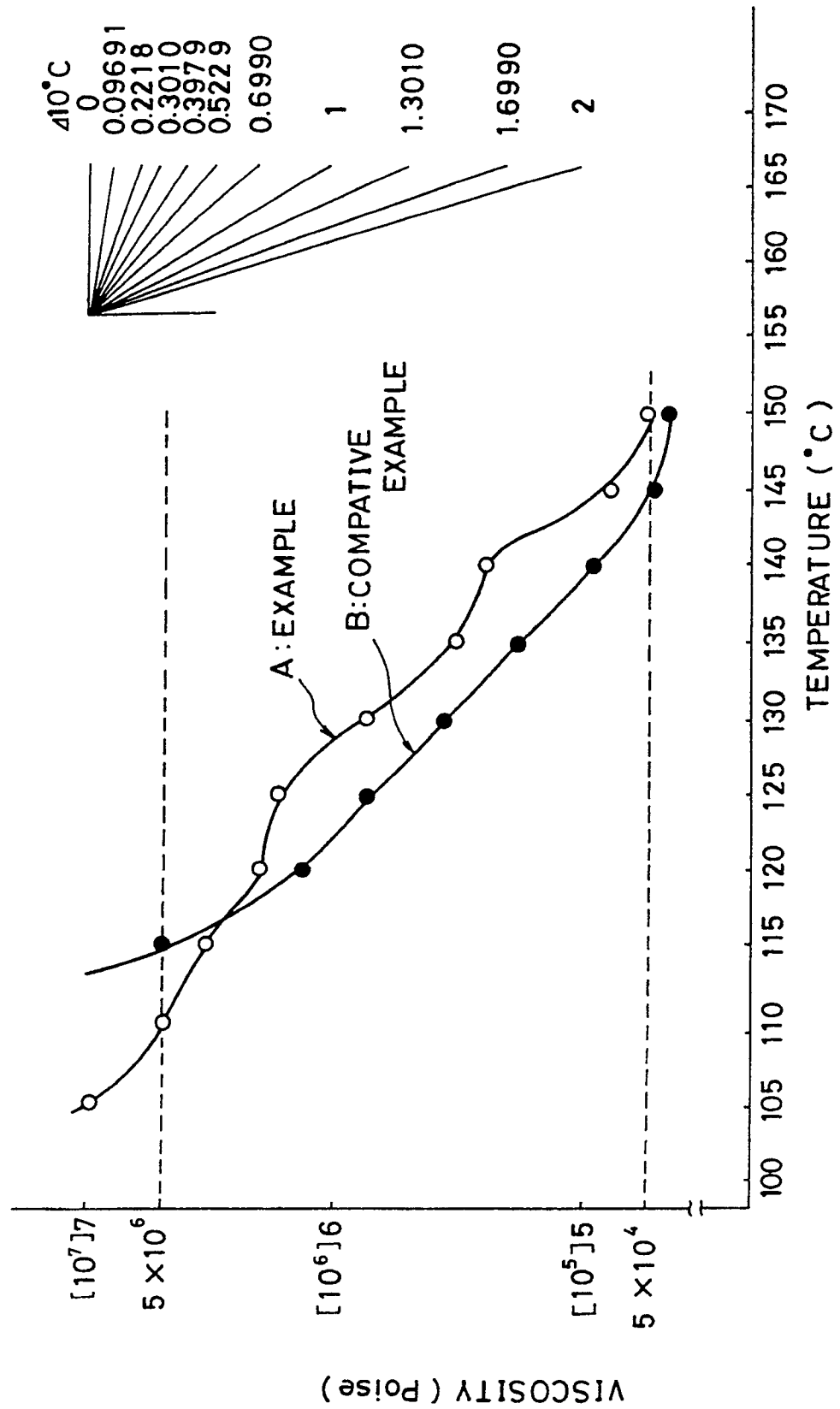


FIG. 2

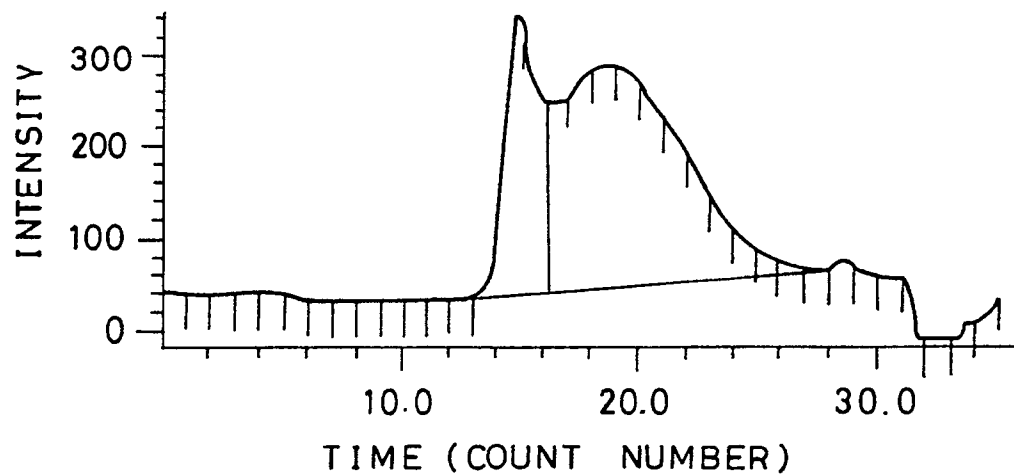


FIG. 3

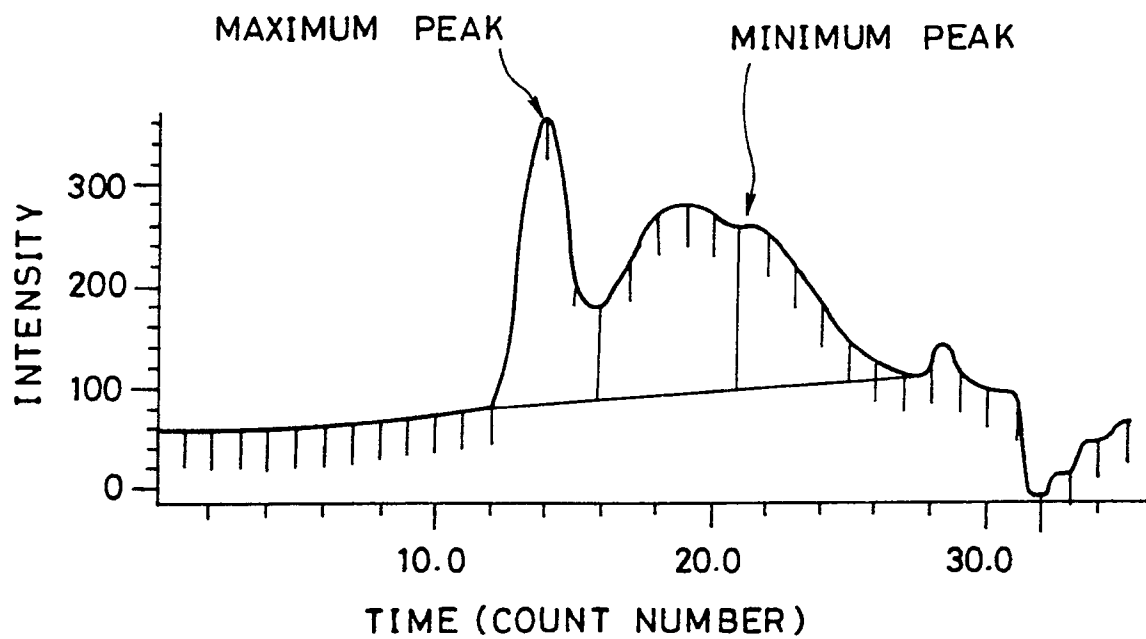
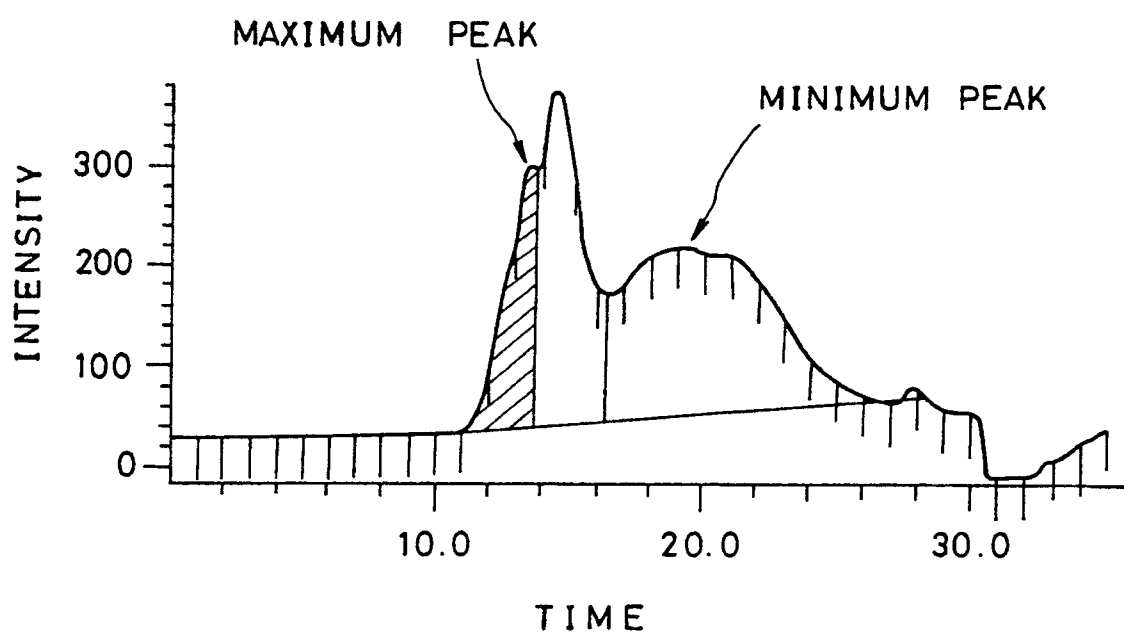


FIG. 4





European Patent
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EUROPEAN SEARCH REPORT

Application Number

EP 90 31 4398

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
P,X	EP-A-0 354 466 (MITSUBISHI RAYON CO.) * Claims; abstract; examples *	1-14	G 03 G 9/08
X	PATENT ABSTRACTS OF JAPAN, vol. 12, no. 460 (P-795)[3307], 5th December 1988; & JP-A-63 183 453 (KYOCERA CORP.) 28-07-1988 * The whole document *	1,2	
X	DE-A-3 027 121 (CANON K.K.) * Claims *	1,2,3,9 10,12-14	
A	EP-A-0 072 176 (KONISHIROKU PHOTO IND. CO.) * Claims; abstract *	3,11	
			TECHNICAL FIELDS SEARCHED (Int. Cl.5)
			G 03 G
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 27-03-1991	Examiner HILLEBRECHT D.A.O.
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