

## DEVELOPER AND DEVELOPING METHOD

2128764

This invention relates to a developer for developing electrostatically charged images in electrostatography including electrophotography, electrostatic recording, electrostatic printing and others and also to a developing method using the same. More particularly, this invention pertains to a developer for electrophotography, which is strongly and uniformly charged to positive charges and is used for visualizing negatively charged electrostatic images to give images of high quality in the direct or indirect electrophotographic developing process, and also to an electrostatographic developing method using the same.

A large number of electrophotographic processes have been known, as disclosed in U.S. Patent 2,297,691 and others. Generally speaking, photoconductive materials are utilized in these processes, and the steps included therein comprise forming electrical latent images on photosensitive members by various means, then developing the latent images by using developing powders (frequently called as "toner"), transferring the toner images thus formed to a recording medium such as paper, as desired, and thereafter

fixing the images by heating, pressure or solvent vapor to obtain copies. When the step of transferring the toner images is applied, it is a general practice to provide a step for removing residual toner on the  
5 photosensitive member.

The developing methods for visualizing electrical latent images by use of toners known in the art may include, for example, the magnetic brush method as disclosed in U.S. Patent 2,874,063; the  
10 cascade developing method as disclosed in U.S. Patent 2,618,552; the powder cloud method as disclosed in U.S. Patent 2,221,776; the method using conductive magnetic toner as disclosed in U.S. Patent 3,909,258; the method using various insulating magnetic toners  
15 as disclosed in Japanese Patent Publication No. 9475/1976; and others.

As the toner for dry development system to be applied for these developing methods, use has heretofore generally been made of fine powder of  
20 natural or synthetic resins having dyes or pigments dispersed therein. For example, a colorant is dispersed in a binder resin such as polystyrene, and the particles obtained by micropulverizing the resultant dispersion into sizes of about 1 to 30 $\mu$  are used as  
25 the toner. As the magnetic toner, magnetic particles are further incorporated into the particles as mentioned above. In case of the system employing the

so called two-component developer, the toner as mentioned above is used generally in mixture with carrier particles such as glass beads, iron particles and others.

5                   In a series of developing methods of electrostatographic processes as mentioned above, wherein electrostatically charged images are developed with a toner charged to the polarity opposite to that of the images, it is very important that the toner  
10                   should be charged to the opposite polarity evenly in order to give good and faithful developing characteristics. For this purpose, it is generally practiced to add a positive or negative charge controller in addition to the above components in order for the  
15                   toner to be charged evenly. Among such charge controllers, positive charge controllers having satisfactory characteristics are very few, while there have been developed some negative charge controllers having good characteristics.

20                   Positive charge controllers conventionally used in toners for dry development system, may include, for example, amino compounds, quaternary ammonium compounds and organic dyes, particularly basic dyes and salts thereof. More specifically, benzyldimethyl-  
25                   hexadecylammonium chloride, decyl-trimethylammonium chloride, nigrosine base, nigrosin hydrochloride, safranine  $\gamma$ , crystal violet and others are known.

Particularly, nigrosine base and nigrosine hydrochloride have been frequently used as positive charge controllers. These dyes are usually added to a thermoplastic resin together with a colorant in the course of formation of a toner to be dispersed in the resin while it is molten under heating, and the resultant resin mixture is micropulverized into fine particles, adjusted to suitable sizes, if desired, and then provided for use as a toner.

10                However, these dyes as charge controllers have complicated structures and do not have constant properties, thus being poor in stability. Also, decomposition or denaturation may occur through decomposition, mechanical collision and friction during kneading underheat or change in temperature and humidity conditions, to cause lowering in the charge controlling characteristic.

20                Accordingly, when development is carried out by use of a toner containing these dyes as charge controllers in a copying machine, the dyes may undergo decomposition or denaturation as the increase in number of copies to cause deterioration of the toner during continual use.

25                As another serious disadvantage, it is very difficult to disperse these dyes as charge controllers evenly into a thermoplastic resin, and their contents in toner particles obtained by pulverization are not

constant to result in different amounts of triboelectric charges among the toner particles. For this reason, in the prior art, various methods have been practiced in order to disperse these dyes more evenly into a resin. For example, a basic nigrosine dye is formed into a salt with a higher fatty acid for improvement of compatibility with a thermoplastic resin. In this case, however, unreacted fatty acid or decomposed product of the salt will be exposed on the toner surfaces to contaminate carriers or toner carrying member and also cause lowering in free flowing properly of the toner, fog and lowering in image density. Alternatively, for improvement in dispersibility of these dyes into a resin, there is also employed a method in which dye powders and resin powders are previously mechanically pulverized and mixed before fusion kneading. This method is not competent enough to overcome the original poor dispersibility, and evenness of charging satisfactory in practical application has not yet been obtained.

Most of dyes for positive charge controlling are hydrophilic and therefore, due to poor dispersibility of these dyes into a resin, the dyes are exposed on the toner surfaces when pulverized after fusion kneading. When the toner is used under highly humid conditions, a drawback that no image of good quality can be obtained, is encountered because of

hydrophilic nature of the dye.

Thus, when a dye having positive charge controlling characteristic of the prior art is used in a toner, variances in amount of the charges generated on the toner particle surfaces through friction among toner particles, between toners and carriers or between toners and toner carrying member such as sleeve, will occur, whereby various inconveniences are caused, such as development fog, toner scattering, carrier contamination, etc. These difficulties become marked when a large number of copying cycles were carried out continuously, giving the results essentially unsuitable for a copying machine.

Also, when the toner containing a positive charge controlling dye is used, the transfer efficiency of the toner image is markedly lowered under highly humid conditions to be unsuitable for practical use. Even under normal temperature and humidity, when the toner is stored for a long time, due to instability of the positive charge controlling dye employed, toner particles may frequently agglomerate to become useless.

As a method for obtaining a positive charge controlling developer, there is a proposal as disclosed in Japanese Patent Publication No. 22447/1978. This is a method in which metal oxide particles treated with aminosilanes are incorporated as a constituent of the developer. However, as the result of my investigation

on this method, when developers were obtained according to the examples disclosed in the Japanese Patent by applying treatments on metal oxides such as colloidal silica, alumina, titanium dioxide, zinc oxide, iron oxide,  $\gamma$ -ferrite, magnesium oxide, etc., no developer exhibiting satisfactory characteristics in practical application could be obtained in any of the combinations, but such a developer was found to have some drawbacks.

10                   Thus, most of the developers thus prepared cannot maintain the preferable characteristics for faithful reproduction of latent images. Although desirable performance may be exhibited at the initial stage, it cannot be maintained in continuous use for  
15 a long term to make the developer useless. More specifically, fog is formed with scattering of the toner around the edges in copying of line images, and the image density is also lowered.

20                   As other drawbacks, when developing and transfer are conducted under the conditions of higher temperature and humidity, and lower temperature and humidity, lowering in image density, scattering of line images, drop-off of images, fog, etc., are encountered. These phenomena are observed in both  
25 developing step and transfer step.

                  As still another drawback, the developer cannot be stored for a long term. Thus, when the

( developer is placed under non-used state for a long time, the characteristics at the initial stage are lowered so that the developer is no longer useful.

Various causes for these drawbacks may be  
5 thought of, but, as the result of my studies (about the above phenomena, the primary cause was found to be that the distribution in amount of the triboelectric charges of the thus obtained developer was broad and not uniform. In connection with this point, a  
10 slightly detailed explanation is given below. J

According to the developing methods known in the art, the forces applied on the developer particles are electrostatic attracting force toward latent image and, sometimes electrical forces from  
15 outside, image force toward the carriers or the toner carrying member such as a developing sleeve, and adhering or agglomerating forces, and adhesion of the developer particles to the latent image is effected through the total contribution of these forces.

20 Accordingly, the state of triboelectric charge assumed by the developer particles will have important effects on the behaviors of the developer particles during the developing step. On the other hand, the developer containing metal oxide powders such as fine silica  
25 powders treated only with an aminosilane compound as described above, cannot maintain in most cases its preferable characteristics for faithful reproduction

of latent images, and the distribution in amount of triboelectric charges of the developer becomes very broad. The above mentioned distribution in amount of triboelectric charges is also broad, even when the  
5 kind or the amount of the aminosilane compound used for treatment of fine silica powder's may be varied, only to give a developer which includes components having smaller triboelectric charges and components having extremely great triboelectric charges after  
10 friction with carriers or a toner carrying member such as a developing sleeve. There also exist a slight quantity of components charged to opposite polarity with a greater value. (see Comparative Example 2A and Fig. 3(a), shown below)

15 In such a developer having a broad distribution of triboelectric charges, the developer components with smaller charge may cause fog or scattering at the edge portion of the latent image, and similar effects may also be incurred by the components charged to  
20 opposite polarity. On the other hand, the developer components with greater charge may be affected by increased image force applied from carriers or a toner carrying member such as developing sleeve may not be readily used for developing, whereby lowering of image  
25 density or coarsening may undesirably be caused.

The distribution in amount of triboelectric charges of such a developer containing fine silica

powder treated only with an aminosilane compound is also susceptible to changes in environmental conditions and will become a distribution unsuitable for development particularly at higher temperature and humidity conditions and lower temperature and humidity conditions. Thus, at higher temperature and humidity, the developer components with smaller charge increase (see Comparative Example 2A, Fig. 3(b)) to cause further markedly fog, lowering of image density, scattering at the edge portion of latent image and lowering of transfer efficiency.

At lower temperature and humidity, the developer components with greater charge increase (see Comparative Example 2A, Fig. 3(c)) to cause more markedly lowering of image density, coarsening and fog and result in increased scattering or drop-off during transfer. Particularly at lower temperature and humidity conditions, this tendency will become further marked by continuous use of the developer, and the initial characteristics of the developer cannot be maintained until the developer becomes no longer useful.

The distribution of triboelectric charges herein mentioned refers to a charged quantity to be measured under the state approximate to the developing system employed. For example, in the two-component developing method, the cascade developing system or

the two-component magnetic brush system, charging of the developer particles is effected primarily in the step of contacting with or peeling off from the carrier particle surfaces. Measurement of the distribution in amount of triboelectric charges in such developer systems may be conducted by use of, for example, the method of L.B. Schein et al (J. Appl. Phys. 46, No. 12, P.5140 (1975)), or the method of R.W. Stover et al (1969 Proc. Ann. Conf. Photo. Sci. Engy SPSE P.156) and R.B. Levis et al (4th International Conf. on Electrophoto. Adv. Print P.61 (1981)).

An object of the present invention is to provide a developer which is stable in amount of triboelectric charges caused between toner particles, or between toner and carrier, or between toner and a toner carrying member such as a sleeve in case of one-component development, also sharp and even in distribution in amount of triboelectric charges, and can be controlled to a charged amount suitable for the developing system employed.

Another object of the present invention is to provide a developer capable of permitting development and transfer to be effected faithfully to latent image, that is, capable of providing a high image density with good reproducibility of half tone, without

adhesion of the toner in the background region during development, namely, without fog or scattering of toner around the edge of latent image.

Still another object of the present invention  
5 is to provide a developer, which can maintain the initial characteristics and is free from agglomeration of toners or changes in charging characteristics, even when the developer is used continuously for a long term.

10 Further object of the present invention is to provide a developer capable of reproducing stable images without suffering from influences from temperature and humidity, particularly with high transfer efficiency, being free from scattering or transfer  
15 failure, i.e., drop-off of images, during transfer at higher humidity and lower humidity conditions.

Further, it is also another object of the present invention to provide a developer excellent in storage stability which can maintain the initial  
20 characteristics even after storage over a long term.

Still another object of the present invention is to provide a developing method adapted for repeated copying operations such as continuous operations by use of a developer as mentioned above.

25 Further, still another object of the present invention is to provide a developing method which is stable even against environmental changes such as

under higher temperature and humidity conditions or lower temperature and humidity conditions.

I have studied intensively with an aim to provide a developer for electrostatography, particularly for electrophotography, which is positively chargeable developer capable of being strongly and evenly charged positively and giving an image of high-quality through visualization of a negatively charged electrostatic image, by overcoming various problems involved in the positively charged toner of the prior art as described above. As a consequence, the developer of the present invention has been attained.

The developer according to the present invention comprises a binder resin, a colorant and a positive charge controller, the positive charge controller comprising fumed silica particles treated with a coupling agent having a hydrolyzable group and a non-hydrolyzable organic group bonded to a tetravalent center atom of Si or Ti and having a hydrophobicity within the range of from 30 to 80 as measured by the methanol titration test.

The developing method according to the present invention employs the above developer which is made insulating and magnetic, and comprises providing an electrostatic image bearing member for bearing electrostatic images on its surface and a developer carrying member arranged with a predetermined gap

therebetween, permitting the insulating magnetic developer to be carried on the developer carrying member in a thickness thinner than the gap, and transferring the developer to the electrostatic image bearing member thereby to develop the electrostatic images.

Examples of adding fine fumed silica powder to a developer for electrophotography are known in the art. However, even a developer containing a dye having positive charge controlling characteristic is changed to negative in its charging polarity and therefore unsuitable for visualization of negative electrostatic images. This is because fine fumed silica powder will reduce the charges of the positively charged developer or even reverse the charging polarity.

Whereas, I have found that an excellent positive charge controller can be obtained by treating such fumed silica powder with a silane or a titanate type coupling agent and controlling the hydrophobicity to an appropriate level, and that a positively chargeable developer which is stably charged to have high triboelectric charges with sharp and uniform distribution, can be obtained by formulation of the controller in the developer. It has also been found that, by controlling both the degree of treatment with the coupling agent and the hydrophobicity, the amount

of the triboelectric charge of the toner containing the resultant positive charge controller as well as its distribution can be controlled to a considerable extent.

5                   It has not yet been clarified in detail why the developer of the present invention has sharp and uniform distribution in amount of triboelectric charges (see Example 1A and Fig. 2(a) to (c)) (probably due to stabilization at a certain equilibrated value  
10 between the leak of excessive charges and charge accumulation through the interaction between the coupling agent and the hydrophobicity modifying agent). Anyway, it has been confirmed that there are few components in the developer having deleterious in-  
15 fluences on development and transfer, and the distribution and of triboelectric charges are little changed even under the conditions of higher temperature and humidity or lower temperature and humidity.

Fig. 1 shows a sectional view showing an  
20 embodiment of the developing step according to the method of this invention.

Fig. 2(a) to Fig. 2(c) and Fig. 4(a) to Fig. 4(c) are graphs showing distributions in amount of triboelectric charges under various conditions in  
25 Example 1A and 1B as described below.

Fig. 3(a) to Fig. 3(c) are graphs showing distributions in amount of triboelectric charges under various conditions in Comparative Example 1A as described below.

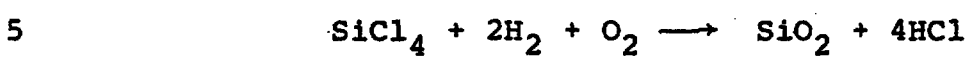
5            Fig. 5 to Fig. 8 are graphs each showing toner weight changes per unit area in the toner layers during successive copying test under the environment of 10°C and 10% R.H., A showing the results of an Example and B that of a Comparative Example in each  
10        case. The respective Figures show the results of the following examples.

          Fig. 5: Example 1F, Comparative Example 3F;  
          Fig. 6: Example 1G, Comparative Example 3G;  
          Fig. 7: Example 1H, Comparative Example 3H;  
15        Fig. 8: Example 1I, Comparative Example 3I.

In the following description, "%" and "parts" representing quantity ratios are all based on weight, unless otherwise indicated.

          The specific positive charge controller to  
20        be used in the developer of the present invention is obtained from fumed silica. "Fumed silica" used herein refers comprehensively to fine silica powder obtained by vapor phase oxidation of silicon halides, and may also sometimes called as the dry process silica.  
25        The method for preparation of fumed silica is known in

the art, and it can be obtained, for example, by pyrolytic oxidation of gaseous silicon tetrachloride in oxygen-hydrogen flame. The basic reaction scheme may be represented as follows:



In the above preparation step, it is also possible to obtain complex fine powder of silica and other metal oxides by using other metal halides such as aluminum chloride or titanium chloride together  
10 with silicon halides. Thus, in the present specification, "fumed silica" is meant to be inclusive of silica containing metal oxides such as  $\text{Al}_2\text{O}_3$ ,  $\text{TiO}_2$ , etc. derived from these metal halides up to 40%.

It is preferred to use fumed silica particles,  
15 of which mean primary particle size is desirably within the range of from 0.001 to  $2\mu$ , particularly preferably of from 0.002 to  $0.2\mu$ .

Commercially available fumed silica products to be used in the present invention include those sold  
20 under the trade names as shown below.

|    |                      |        |
|----|----------------------|--------|
| 25 | AEROSIL              | 130    |
|    | (Nippon Aerosil Co.) |        |
|    |                      | 200    |
|    |                      | 300    |
|    |                      | 380    |
|    |                      | TT 600 |
|    |                      | MOX 80 |
|    |                      | COK 84 |

Ca-O-Sil  
(Cabot Co.)

M-5

MS-7

MS-75

HS-5

EH-5

Wacker HDK N 20  
(WACKER-CHEMIE GMBH)

V 15

N 20E

T 30

T 40

D-C Fine Silica  
(Dow Corning Co.)

Fransol  
(Fransil Co.)

These fumed silica particles may be used as such. More preferably, however, they are subjected once to heat treatment at a temperature of 400°C or higher before subsequent treatment with a coupling agent. By effecting this heat treatment, there can be obtained additional effects that not only the components of the developer obtained having deleterious influences on development and transfer can be removed to further make shaper the distribution in amount of triboelectric charges (see Example 1B and Fig. 4(a) to (c) shown below), but also the reduction in amount of triboelectric charges is very small without substantial lowering in quality of copying even if the developer is stored for a long term under the conditions

of high temperature and high humidity. This may be attributable to the following reason. That is, fumed silica, namely, fine silica particles formed by vapor phase oxidation of a silicon halide compound, have  
5 a large number of hydroxyl groups formed on their surfaces. These hydroxyl groups may be classified into the several kinds as mentioned below.

1. Silanol groups on the surfaces: these groups have no possibility of mutual interaction within their  
10 acting regions, because they are spacially made apart from other silanol groups, and therefore called as "lone" or "free" silanol groups;

2. The same kind of groups per se as 1 above, with proviso that these groups are approximated so  
15 as to be capable of interaction through hydrogen crosslinking, and therefore may be called as "bonded (hydrogen crosslinked) silanol groups";

3. Hydroxyl groups of water adsorbed on the surfaces.

20 When fumed silica particles are subjected to the heat treatment at 400°C or higher, condensation will occur mutually between the silanol groups among these hydroxyl groups on the silica surfaces, to result in stabilization of the surface. When heat treated  
25 at a temperature below 400°C, the adsorbed water is removed to reduce the water content in the fumed silica, but when returned to normal temperature, it absorbs

again water to a water content equal to that before heat treatment. However, when treated at a temperature of 400°C or higher, water is liberated through condensation of the hydroxyl groups on the surface, and therefore the water content becomes markedly smaller as compared with that before the heat treatment, even when returned to normal temperature. Although the hydroxyl groups cannot completely be removed, the residual number of hydroxyl groups is convenient for hydrophobicity modification treatment which is to be effected as the post-treatment, if desired.

The heat treatment may be conducted by, for example, leaving fine silica powder to stand in an electric furnace at a temperature of 400°C or higher for a suitable length of time. So far as the characteristics of the developer are not markedly lowered, the heat treatment method is not particularly limited, but any desirable method can be employed. The heat treatment temperature may be preferably 450°C to 1500°C, particularly 500°C to 1000°C.

The time for the heat treatment may vary depending on the treatment temperature, the sizes of the fumed silica particles and other characteristics, but generally range from one minute to 10 hours, particularly from 10 minutes to 10 hours, which can be determined with a measure that the hygroscopicity as the result of the heat treatment may become 5% or below

(particularly 3% or below). The hygroscopicity is measured by subjecting the heat-treated fumed silica particles to standing on a saturated aqueous solution with sodium thiosulfate at the bottom, i.e. in a  
5 humidity of 78%, for about one week and thereafter to measurement of the heating reduction curve from normal temperature to 400°C by means of a thermobalance, and determining its reduced quantity as the hydroscopicity.

10 For obtaining the developer of the present invention, the fumed silica, optionally subjected to the heat treatment as described above, is treated with a coupling agent. The coupling agent used herein comprises a silane type or titanate type coupling  
15 agent, having a hydrolyzable group and a non-hydrolyzable organic group bonded to the tetravalent center atom of Si or Ti.

For example, the silane type coupling agent may include those represented by the formula (1)  
20 shown below:

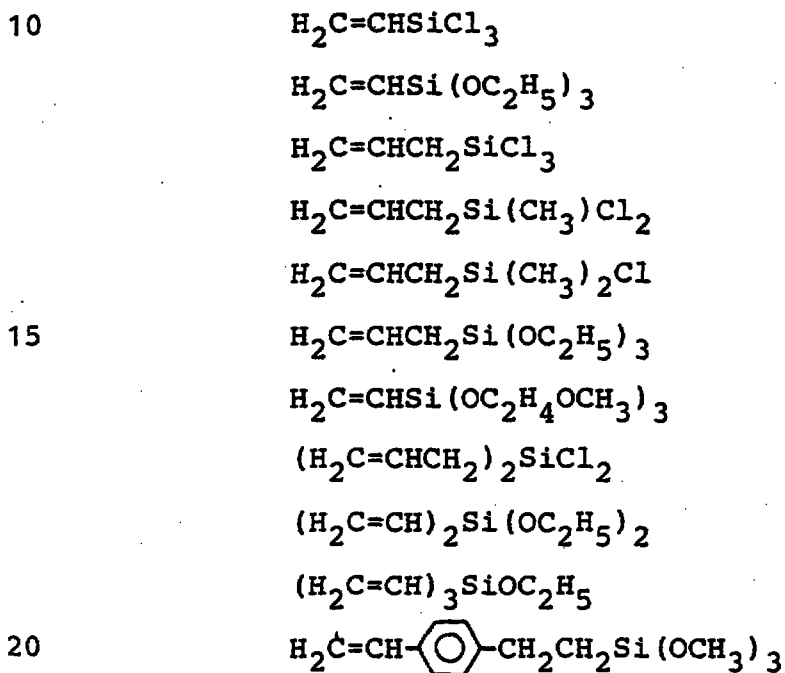


wherein R is an alkoxy group having 1 to 10 carbon atoms such as methoxy, ethoxy, propoxy, isopropoxy, butoxy, isobutoxy, pentyloxy and the like  
25 groups, or a chlorine atom; m and n are integers satisfying the relation of m + n = 4; Y is an organic group containing at least one of amino, vinyl, glycidoxy,

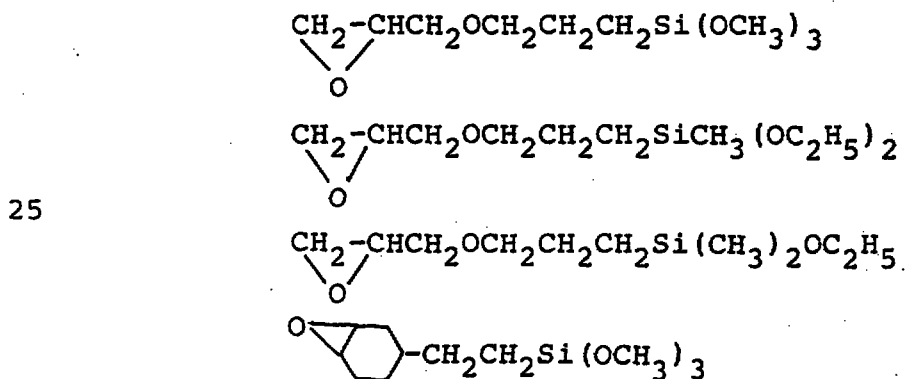
mercapto, methacryl, and ureido groups, particularly a hydrocarbyl group in which a part of the hydrogen atoms can be further substituted with a carbonyl, ether, ester or imino group; with proviso that a plurality of R and Y existing in the same compound may be the same or different.

Typical examples of the coupling agents of the formula (1) are enumerated below.

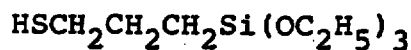
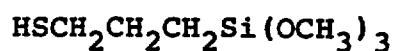
Compounds having vinyl group:



Compounds having glycidoxy group:

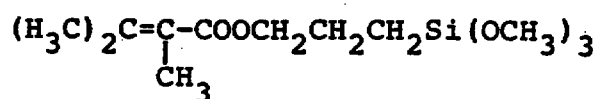
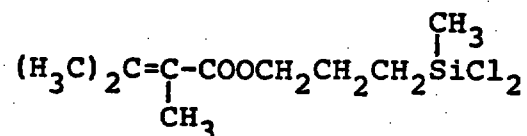


Compounds having mercapto group:

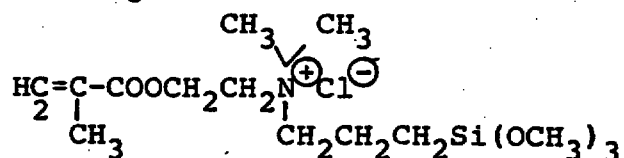
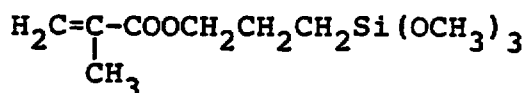


Compounds having methacryl group:

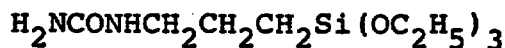
5



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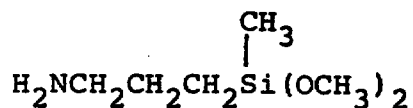
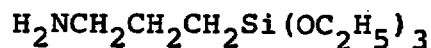


15 Compounds having ureido group:

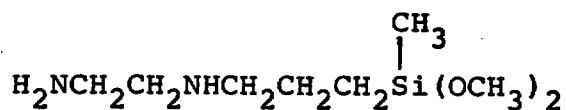


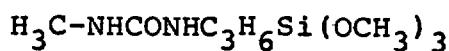
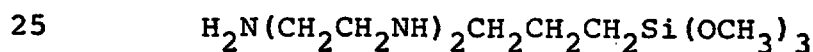
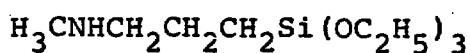
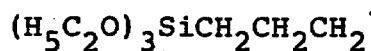
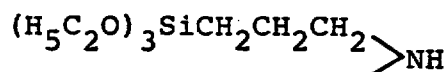
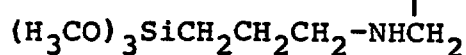
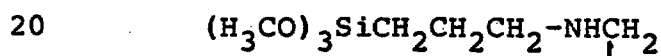
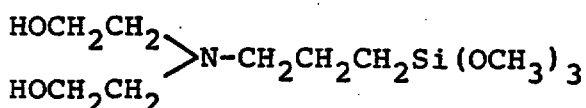
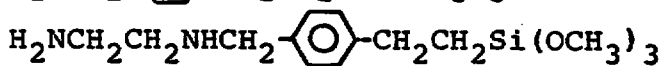
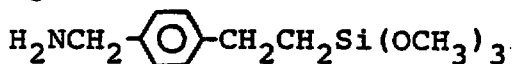
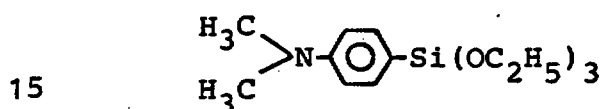
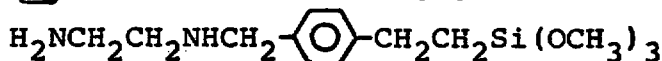
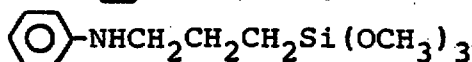
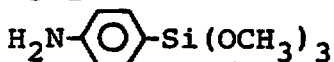
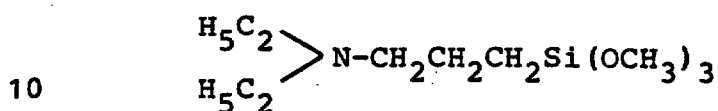
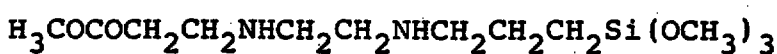
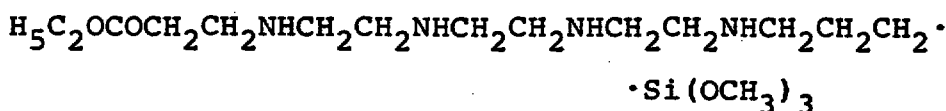
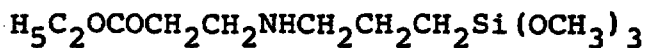
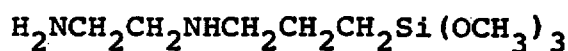
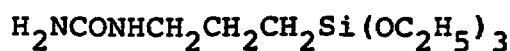
In particular, preferable silane coupling agents to be used in the present invention are compounds having an amino group, examples of which are those

20 having the structural formulas as shown below:



25

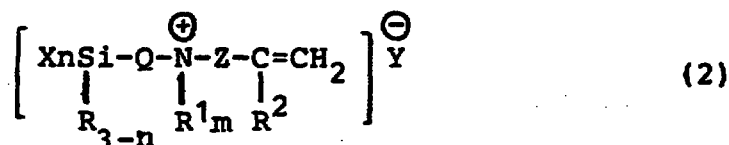




42

In the above compounds, the alkoxy group may be replaced by chlorine atoms.

As another group of silane type coupling agents, there are cation type unsaturated amino-  
5 functional silanes represented by the formula (2) shown below:



10            wherein X is a hydroxyl group or a hydro-  
lyzable group; R is an alkyl having 1 to 6 carbon  
atoms; n is an integer of 1 to 3; Q is a divalent  
hydrocarbon group, or an organic group containing  
oxygen in the form of  $-\text{COC}-$ ,  $-\overset{\text{O}}{\underset{\text{O}}{\text{C}}}\text{C}-$ ,  $-\overset{\text{O}}{\underset{\text{O}}{\text{C}}}-$ , or  $-\overset{\text{O}}{\underset{\text{O}}{\text{C}}}\text{OH}$   
15  
or nitrogen in the form of  $\text{R}^2\text{N}=$  group, the rest, if  
any, of the organic group comprising a hydrocarbon  
unit in most cases;  $\text{R}^1$  is a hydrogen atom, an alkyl  
group having 1 to 6 carbon atoms or a heterocyclic  
20 organic group having nitrogen atom in the ring; m  
is 2; Z is a divalent organic group having a  
double bond conjugated with  $-\text{C}=\text{CH}_2$ , and bonded through  
 $\text{R}^2$   
through C-N bonding to the nitrogen atom on its left  
25 side;  $\text{R}^2$  is a hydrogen atom or an alkyl having 1 to  
6 carbon atoms; and Y is an acid anion.

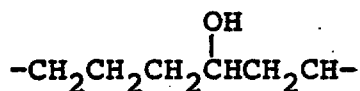
More particularly, X is a hydroxyl group or

a hydrolyzable group such as alkoxy group, aryloxy group, hydrogen atom, acyloxy group, ketooxime group, amino group, etc. The "hydrolyzable group" herein mentioned means a group which can react with water at room temperature to form a silanol.

R is a lower alkyl having not more than 6 carbon atoms. The R groups bonded to the same silicon atom may be the same or different.

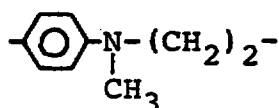
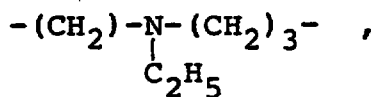
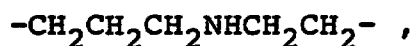
The binding group Q between the silicon atom and the nitrogen atom is constituted of carbon, hydrogen, oxygen or nitrogen, containing oxygen in the form of carbonyl, ether, ester or hydroxyl or containing nitrogen in the form of amide.

Specific examples of Q are divalent hydrocarbon groups, carbonyl groups, ether groups, ester groups or a group having a hydroxyl group as shown below:



Alternatively, Q may also contain nitrogen as shown

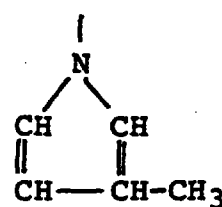
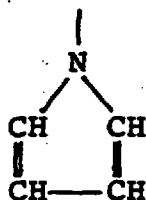
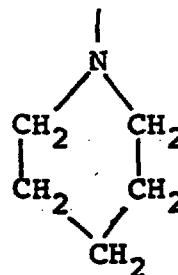
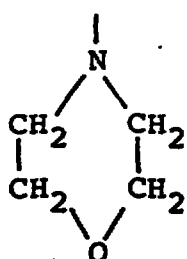
below:



44

$R^1$  is selected independently from the groups such as hydrogen atom, alkyl groups similar to R and heterocyclic groups having nitrogen in the ring as shown below:

5



10 Z is a divalent organic group constituted of carbon, hydrogen and oxygen as mentioned in connection with the group Q, and is further characterised by having a double bond conjugated with a vinyl group. Z is bonded through carbon-nitrogen bonding to the nitrogen group on its left side. Examples of such divalent groups are arylene group, carbonyl group and vinyl group.

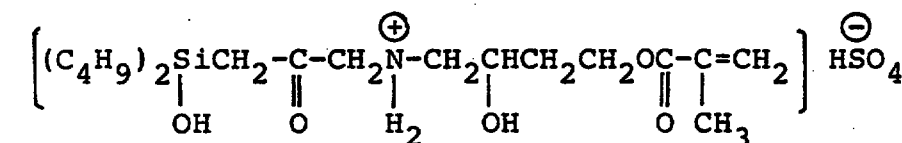
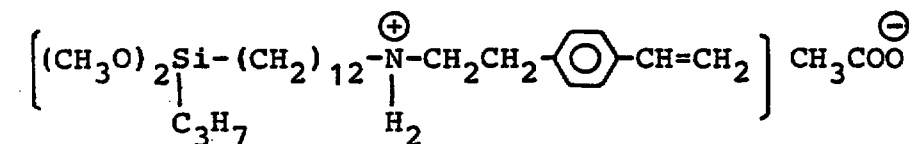
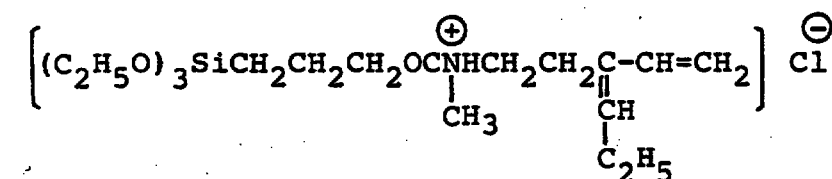
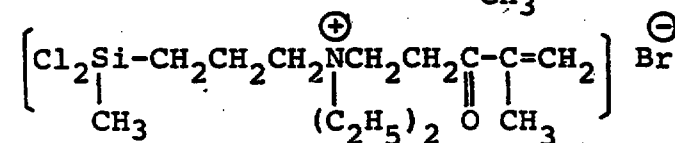
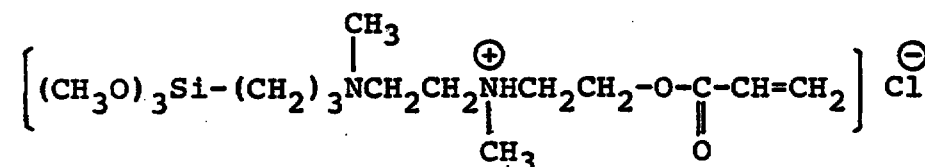
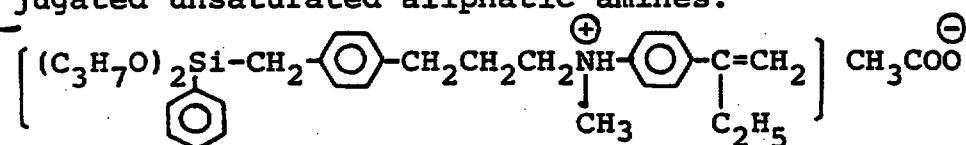
15

$R^2$  is a hydrogen atom or an alkyl having 1 to 6 carbon atoms.

Y is a hydrogen atom; chlorine, bromine,

iodine; or an acidic anion such as carboxylate anion, or, for example, formate anion, acetate anion, phosphate anion, sulfate anion, nitrate anion, etc.

Typical examples of the compounds represented by the above formula (2) are enumerated below. These compounds can be prepared by the reaction between amino functional silanes and conjugated unsaturated alkyl halides. Alternatively, they can also be prepared by the reaction between silicon alkyl halides and conjugated unsaturated aliphatic amines.

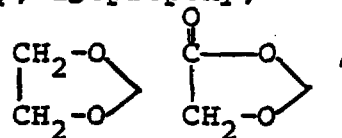


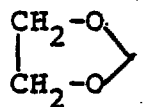
The above cation type unsaturated aminofunctional silane can be also used as its hydrolyzate for treatment of fumed silica.

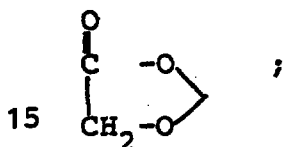
Examples of the titanate type coupling agent  
5 include the compounds represented by the following formula:



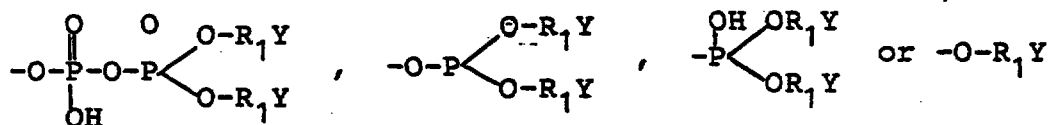
wherein m and n are 1 and 2, 1 and 3, or 4 and 2, respectively; R is an alkoxy having 1 to 10 carbon atoms such as methoxy, ethoxy, propoxy, isopropoxy,  
10 butoxy, isobutoxy, pentyloxy, etc. or



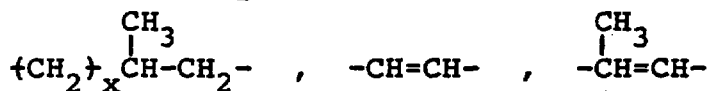
provided that when m is 1 and n is 2, R is  or



X is  $-O-CH_2-R_1Y$ ,  $-O-CO-R_1Y$ ,  $-O-SO_2-R_1Y$ ,  $-O-P(=O)(OR_1Y)(OR_1Y)$

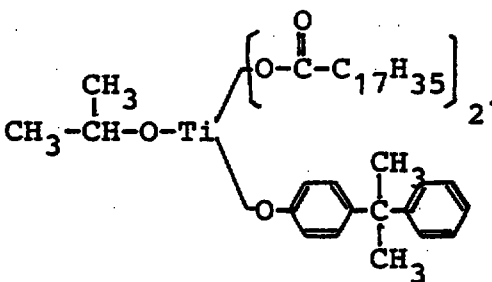
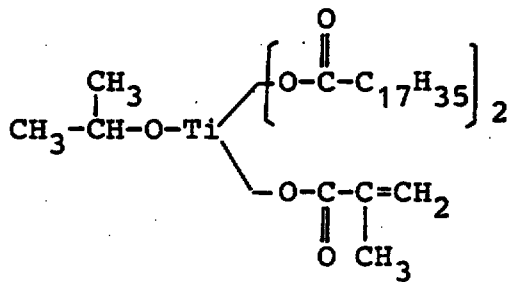
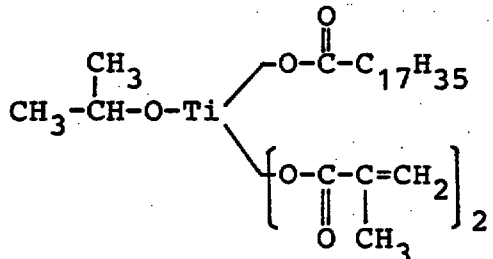


20 (in the above formulae,  $R_1$  is a saturated or unsaturated divalent aliphatic group having 1 to 34 carbon atoms such as  $\{CH_2\}_x$ ,

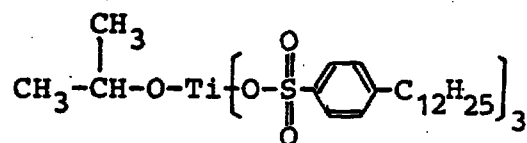


25 where  $x$  is an integer of 1 to 31, or a divalent aromatic hydrocarbylene group; Y is a hydrogen atom or an amino group; and a plurality of X,  $R_1$  and Y existing in the same compound being the same or different, respectively).

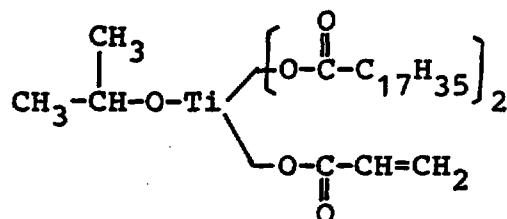
Typical examples of the titanate type coupling agents may include those as enumerated below:

| <u>Chemical name</u>                         | <u>Chemical structure</u>                                                                                                                                                   |
|----------------------------------------------|-----------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| Isopropyl tristearoyl                        | $\text{CH}_3-\overset{\text{CH}_3}{\underset{ }{\text{CH}}}-\text{O}-\text{Ti}\left\{\text{O}-\overset{\text{O}}{\parallel}{\text{C}}-\text{C}_{17}\text{H}_{35}\right\}_3$ |
| Isopropyl trioctanoyl titanate               | $\text{CH}_3-\overset{\text{CH}_3}{\underset{ }{\text{CH}}}-\text{O}-\text{Ti}\left\{\text{O}-\overset{\text{O}}{\parallel}{\text{C}}-\text{C}_7\text{H}_{15}\right\}_3$    |
| Isopropyl diisostearoyl cumylphenyl titanate |                                                                                          |
| Isopropyl distearoyl methacryl titanate      |                                                                                         |
| Isopropyl dimethacryl isostearoyl titanate   |                                                                                         |

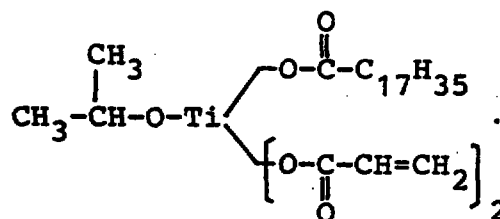
Isopropyl tridodecylbenzene  
sulfonyl titanate



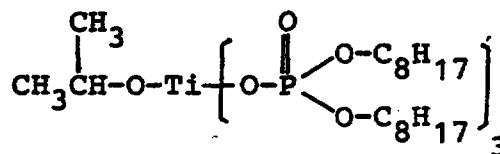
Isopropyl diisostearoyl  
acryl titanate



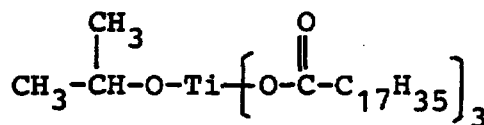
Isopropyl diisostearoyl  
diacryl titanate



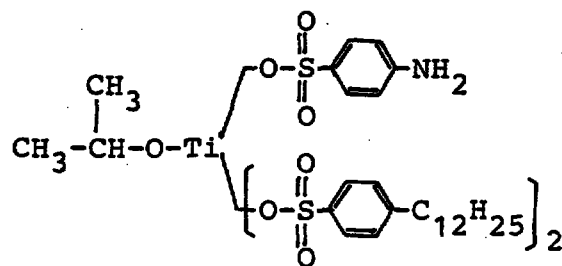
Isopropyl tri(dioctyl-  
phosphate) titanate



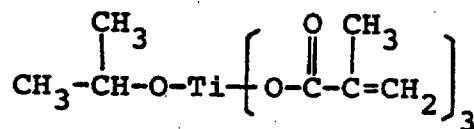
Isopropyl tri-n-  
stearoyl titanate



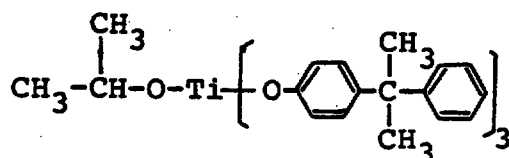
Isopropyl 4-aminobenzene  
sulfonyl di(dodecyl-  
benzenesulfonyl) titanate



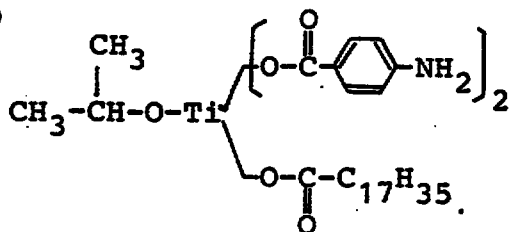
Isopropyl trimethacryl  
titanate



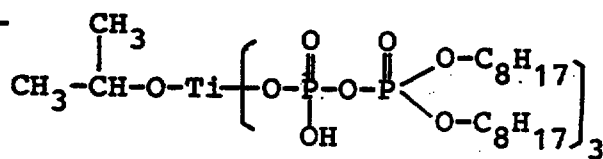
Isopropyl tricumylphenyl  
titanate



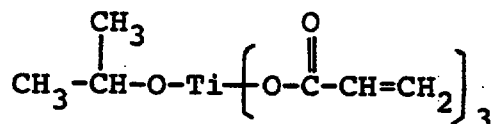
Isopropyl di(4-aminobenzoyl)  
isostearoyl titanate



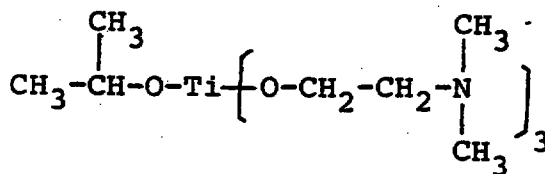
Isopropyl tri(dioctylpyro-  
phosphate) titanate



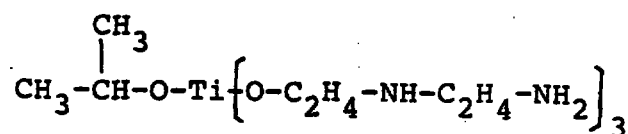
Isopropyl triacryl  
titanate



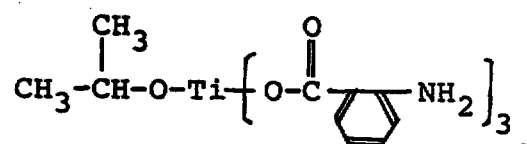
Isopropyl tri(N,N-  
dimethylethylamino)  
titanate



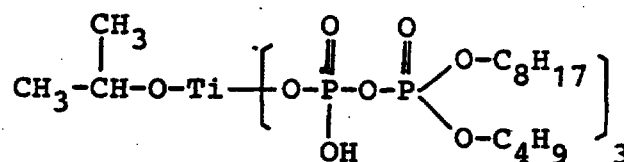
Isopropyl tri(N-ethyl-  
aminoethylamino)  
titanate



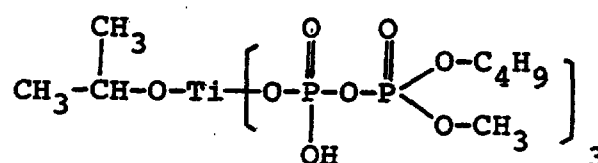
Isopropyl trianthranyl  
titanate



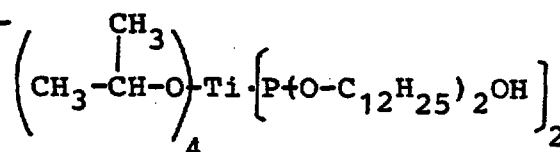
Isopropyl octyl, butyl  
pyrophosphate titanate



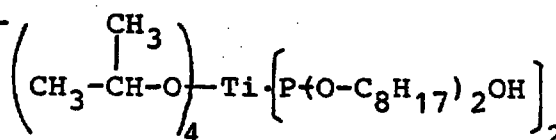
Isopropyl di(butyl,  
methyl pyrophosphate)  
titanate



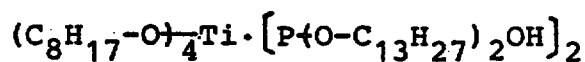
Tetraisopropyl di(lauryl-  
phosphite)titanate



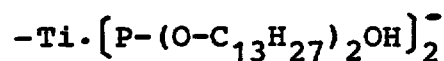
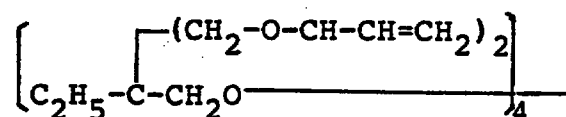
Tetraisopropyl di(octyl-  
phosphite)titanate



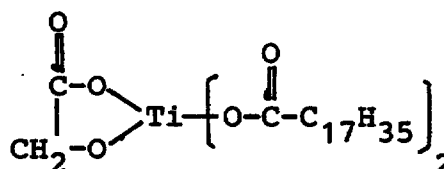
Tetraoctyl di(tridecyl-  
phosphite)titanate



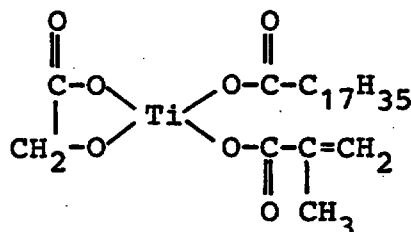
Tetra(2,2-diallyloxymethyl-  
1-butoxy)-di-(di-tridecyl)-  
phosphite titanate



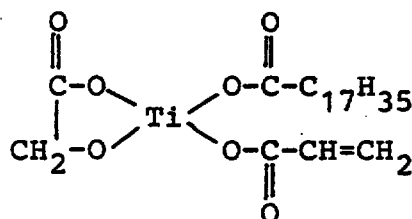
Diisostearoyl oxyacetate  
titanate



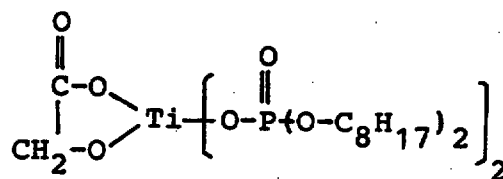
Isostearoyl methacryl  
oxyacetate titanate



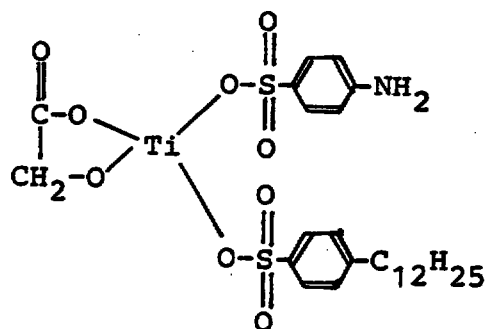
Isostearoyl acryl  
oxyacetate titanate



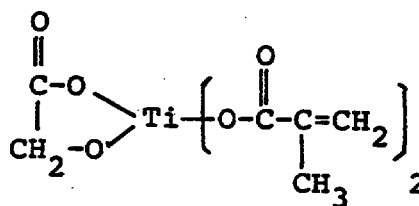
Di(dioctylphosphate)-  
oxyacetate titanate



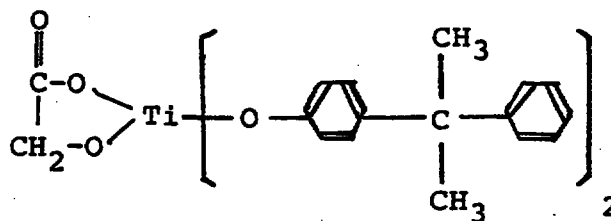
4-Aminobenzenesulfonyl-  
dodecylbenzenesulfonyl-  
oxyacetate titanate



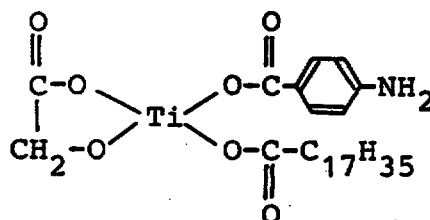
Dimethacryl oxyacetate  
titanate



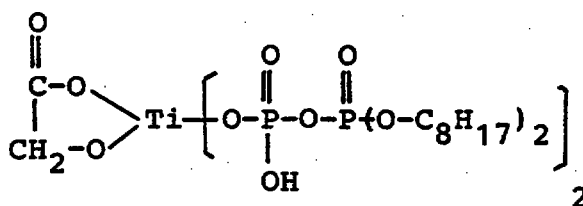
Dicumylphenolate  
oxyacetate titanate



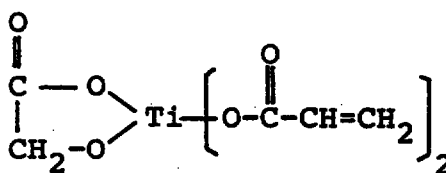
4-Aminobenzoyliso-  
stearoyl oxyacetate  
titanate



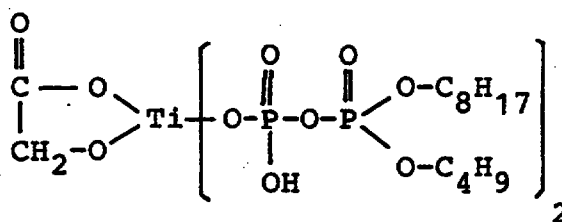
Di(dioctylpyrophos-  
phate) oxyacetate  
titanate



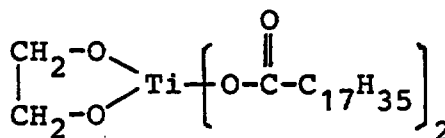
Diacryl oxyacetate  
titanate



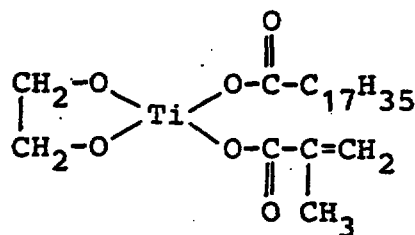
Di(octyl, butylpyro-  
phosphate) oxyacetate  
titanate



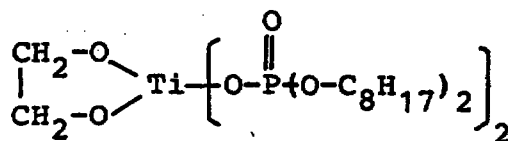
Diisostearoyl ethylene  
titanate



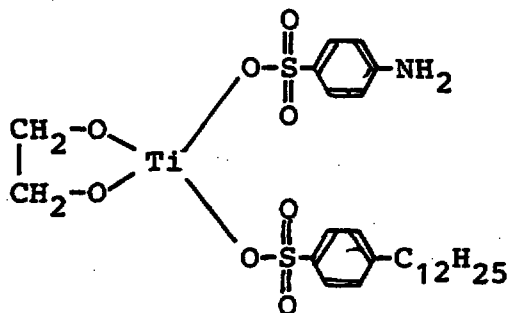
Isostearoyl methacryl-  
ethylene titanate



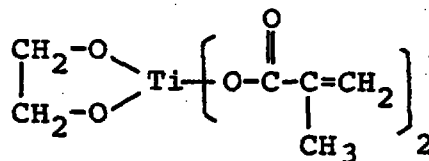
Di(dioctylphosphate)  
ethylene titanate



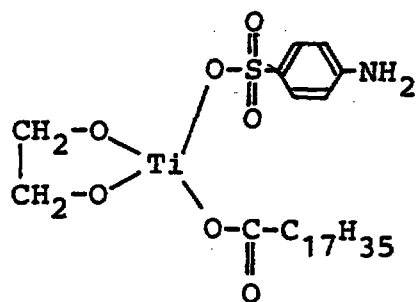
4-Aminobenzenesulfonyl-  
dodecylbenzenesulfonyl  
ethylene titanate



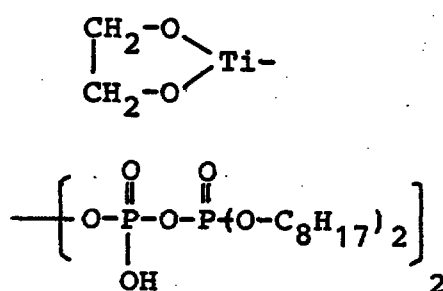
Dimethacryl ethylene  
titanate



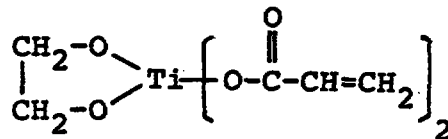
4-Aminozenzoyl isostearoyl  
ethylene titanate



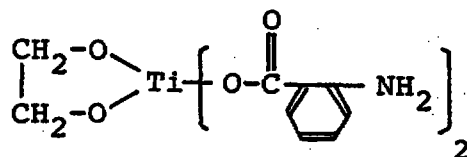
Di(dioctylpyrophosphate)  
ethylene titanate



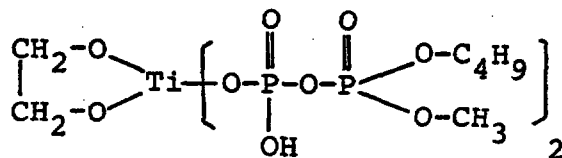
Diacryl ethylene  
titanate



Dianthranyl ethylene  
titanate



Di(butyl,methylpyro-  
phosphate)ethylene  
titanate



The silane type or titanate type coupling agent as described above may be employed alone, or alternatively, two or more kinds of coupling agents selected from one or two types can be used as a mixture.

5           As the method for treating the fumed fine silica particles with a coupling agent, it is possible to use a wide scope of treating methods of both dry and wet methods, because the coupling agent to be used in the present invention reacts readily with the bonded water possessed chemically or physically exist-  
10           ing on the surfaces of fine silica particles to be covered thereon. For example, into a mixing machine such as a Henschel mixer or a ball mill, fine silica particles and an appropriate amount of a coupling  
15           agent may be charged, and dry mixing is carried out. Alternatively, a coupling agent may be dissolved in a suitable solvent, and fine silica particles are charged into the resultant solution, followed by mixing, and thereafter the solvent is removed.  
20           Various other methods may also be available.

A coupling agent may be used for the treatment at a proportion of 0.01 to 20% (preferably 0.1 to 10%) based on the fine silica particles.

In order that the charge controller of the  
25           present invention can have a desired positive charging controlling characteristic, it is required to have a value of hydrophobicity within the range from 30

to 80, as measured by the methanol titration test. The "methanol titration test" defined in the present invention for evaluation of hydrophobicity is conducted as follows.

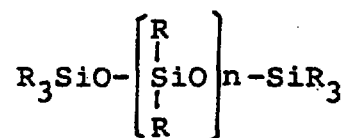
5           Sample fine silica particles (0.2 g) are charged into 50 ml of water in a 250 ml-Erlenmeyer's flask. Methanol is added dropwise from a buret until the whole amount of the silica is wetted therewith. During this operation, the content in the flask is  
10 constantly stirred by means of a magnetic stirrer. The end point can be observed when the total amount of the fine silica particles is suspended in the liquid, and the hydrophobicity is represented by the percentage of the methanol in the liquid mixture of  
15 water and methanol based on the quantity of methanol added on reaching the end point.

—           The fumed silica particles treated with a coupling agent as described above have a hydrophobicity within the range as specified above, when the coupling  
20 agent employed is a titanate type. However, when treated with a silane type coupling agent alone, the resultant particles will lack in sufficient hydrophobicity. Accordingly, in this case, the hydrophobicity is required to be controlled within the  
25 range from 30 to 80 by use of an appropriate hydrophobicity modifier. As such a method for hydrophobicity modification, there may be used any method known in

the art, but it is preferred to use as the hydrophobicity modifier an organic silicon compound reactive with or capable of being physically adsorbed onto fumed fine silica particles or an silicone oil capable of wetting and covering the fumed silica particles.

Example of the organic silicone compounds include: hexamethyldisilazane, trimethylsilane, trimethylchlorosilane, trimethylethoxysilane, dimethyldichlorosilane, methyltrichlorosilane, allyldimethylchlorosilane, allylphenyldichlorosilane, benzyldimethylchlorosilane, bromomethyldimethylchlorosilane,  $\alpha$ -chloroethyltrichlorosilane,  $\beta$ -chloroethyltrichlorosilane, chloromethyldimethylchlorosilane, triorganosilylmercaptan, trimethylsilylmercaptan, triorganosilyl acrylate, vinyl dimethylacetoxysilane, and further dimethylethoxysilane, dimethyldimethoxysilane, diphenyldiethoxysilane, hexamethyldisiloxane, 1,3-divinyldimethyltetramethyldisiloxane, 1,3-diphenyldimethyltetramethyldisiloxane, and dimethylpolysiloxanes having 2 to 12 siloxane units per molecule and containing each one hydroxyl group bonded to Si at the terminal units and the like. These may be used alone or as a mixture of two or more compounds.

The silicone oil is represented by the formula:



— As preferable silicone oils, those having viscosities of about 5 to 5000 centistokes at 25°C may be used, including as preferable examples methyl silicone oil, dimethyl silicone oil, phenyl methyl  
5 silicone oil, chlorophenyl methyl silicone oil, alkyl-  
modified silicone oil, fatty acid-modified silicone oil, polyoxyalkylene-modified silicone oil and the like. These may be employed singly or in combination.

The hydrophobicity modification may be  
10 carried out by treating the fumed silica particles with a hydrophobicity modifier after treatment of the fumed silica particles with a coupling agent as described above or by treating the fumed silica  
particles with a mixture of a coupling agent and a  
15 hydrophobicity modifier.

To describe about the treatment method, for example, the above treating agent for hydrophobicity modification (in some cases, a mixture of this agent with a coupling agent), optionally diluted with a  
20 suitable solvent, may be directly mixed with silica particles by a mixer such as Henschel mixer, or sprayed onto silica particles. If desired, drying is performed after the treatment to remove the solvent.

The preferable weight ratio of the coupling  
25 agent (particularly of the silane type) to the hydrophobicity modifier is within the range of 15:85 to 85:15, and the value of the triboelectric charge of

the resultant developer containing the charge controller can be controlled to a desired value by varying the ratio within said range. Suitable mixing ratio also depends on the kinds of the coupling agent and  
5 the hydrophobicity modifier employed. The total quantity of the coupling agent and the hydrophobicity modifier may be preferably 0.1 to 30%, more preferably 0.5 to 20%, of the fumed silica particles.

The binder resin for the toner of the  
10 present invention may be composed of homopolymers of styrene and derivatives thereof such as polystyrene, poly-p-chlorostyrene, polyvinyltoluene, and the like; styrene copolymers such as styrene-propylene copolymer, styrene-vinyltoluene copolymer, styrene-vinylnaphtha-  
15 lene copolymer, styrene-methyl acrylate copolymer, styrene-ethyl acrylate copolymer, styrene-butyl acrylate copolymer, styrene-octyl acrylate copolymer, styrene-methyl methacrylate copolymer, styrene-ethyl methacrylate copolymer, styrene-butyl methacrylate  
20 copolymer, styrene- $\alpha$ -chloromethyl methacrylate copolymer, styrene-acrylonitrile copolymer, styrene-vinyl methyl ether copolymer, styrene-vinyl ethyl ether copolymer, styrene-vinyl ethyl ketone copolymer, styrene-butadiene copolymer, styrene-isoprene copolymer,  
25 styrene-acrylonitrile-indene copolymer, styrene-maleic acid copolymer, styrene-maleic acid ester copolymer, and the like; polymethyl methacrylate, polybutyl

methacrylate, polyvinyl chloride, polyvinyl acetate, polyethylene, polypropylene, polyesters, polyurethanes, polyamides, epoxy resins, polyvinyl butyral, polyacrylic acid resin, rosin, modified rosins, terpene resin, phenol resins, aliphatic or alicyclic hydrocarbon resins, aromatic petroleum resin, chlorinated paraffin, paraffin wax, etc. These binder resins may be used either singly or as a mixture.

As the colorant to be used in the toner of the present invention, pigments or dyes known in the art such as carbon black, iron black, etc. may be employed. When the magnetic materials as described hereinafter have sufficiently dense color, these materials can substitute for at least a part of the colorant. It is also possible and preferable for imparting a stable positive charge controlling effect to use a dye known as a positive charge controller in the art in combination with the charge controller as described above of the present invention. For example, various dyes such as benzyldimethyl-hexadecylammonium chloride, decyl-trimethylammonium chloride, nigrosine base, nigrosine hydrochloride, safranine  $\gamma$  and crystal violet, may be used.

The developer (toner) of the present invention can be obtained by formulating the positive charge controller as prepared above into a toner comprising binder particles having at least a colorant

dispersed therein. The amount of the positive charge controller may be 0.01 to 20% based on the total weight of the developer for exhibiting its effect, particularly preferably 0.1 to 3% to exhibit a positive charging characteristic with excellent stability. The charge controller may exhibit a considerable extent of effect when contained in the toner particles, but it is further preferred that 0.01 to 3% based on the developer weight of the treated charge controller particles adhere onto the toner particle surfaces. For example, while the charge controller in a quantity of several to 20% is required to accomplish the desired effect if it is contained in the toner particles, the quantity of 0.01 to 3% is sufficient when it adhere onto the toner particle surfaces. In this sense, it is preferred that the charge controller particles have a mean particle size of 0.001 to  $2\mu$ , particularly 0.002 to  $0.2\mu$ , similarly as the starting fumed silica particles, while the mean particle size of the toner may preferably be 1 to  $100\mu$ , particularly 1 to  $50\mu$ . Such an adhering state of the charge controller can be obtained by adding the charge controller particles to a toner comprising particles of a binder resin and at least a colorant dispersed therein and mixing them in a dry powder mixer utilizing a shearing force such as a Henschel mixer. The charge controller may be caused

to adhere onto the toner particles which already contain another part of the charge controller inside.

In order to use the toner of the present invention in the form of a magnetic toner, magnetic powder may also be incorporated therein.

The magnetic powder to be incorporated in the toner may be of strongly magnetic elements and alloys or compounds containing them, including those known as magnetic materials such as alloys or compounds of iron, cobalt, nickel, manganese, etc. as exemplified by magnetite, hematite, ferrite, and other strongly magnetic alloys. The magnetic powder conventionally used may have a mean particle size of from 0.05 to 5 $\mu$ , preferably 0.1 to 1 $\mu$ . The magnetic powder may preferably be contained in an amount of 10 to 70%, more preferably 15 to 35%, based on the toner including the magnetic powder.

Further, the toner of the present invention can be mixed with carrier particles, if desired, such as iron powder, glass beads, nickel powder, ferrite powder, etc. to be used as a developer for electrostatic latent images.

The developer of the present invention is applicable to various developing methods adopted in processes generally called comprehensively as electrostatographic processes. For example, it is applicable to the magnetic brush developing method, the cascade

developing method, the method as disclosed in U.S. Patent 3,909,258 in which conductive magnetic toner is used, the method as disclosed in Japanese Laid-open Patent Application No. 31136/1978 in which high resistivity magnetic toner is used, the methods as disclosed in Japanese Laid-open Patent Applications Nos. 42121/1979, 18656/1980 and 43027/1979, the fur brush developing method, the powder cloud method, the impression developing method, and others.

10                However, one of the most attractive methods for utilizing the developer according to the present invention is that in which it is used in the form of an insulating, i.e., electro-nonconductive, magnetic developer (jumping developer) in a developing method, 15 which comprises providing an electrostatic image bearing member for bearing electrostatic images on its surface and a developer carrying member such as a rotating sleeve arranged with a predetermined interval therebetween at the developing station, 20 having an insulating magnetic developer carried in a thickness thinner than said interval on the developer carrying member, and transferring said developer to the aforesaid electrostatic image holding member at the developing station thereby to effect development, 25 as disclosed in Japanese Laid-open Patent Application No. 43027/1979 or No. 18656/1980. The reasons are as follows. Thus, the above developing method

belonging to the one-component developing methods is free from a drawback inherent to the two-component method employing carrier particles and toner particles that the image quality or the density may vary due to the charge in quantity proportions between these two kinds of particles and also has an excellent feature that toner image formation stable and faithful to the electrostatic image can be obtained, due to formation of a uniform and thin toner layer facing the electrostatic image bearing member, which enables uniform migration of the toner toward the electrostatic image. According to my observation, however, when copying is repeated by use of a jumping developer known in the art, evenness of the developer layer carried on the developer bearing member may sometimes be impaired, for example by formation of toner layer in streaks along the circumferential direction of the carrying member, local extreme increase in thickness of the developer layer carried as compared with the initial thickness, which may result in generation of spot-like irregularities or formation of ripples. The first irregularity may be observed as white streaks on the image when developed, while the second may be observed as density irregularities in the form of spots and the third as ripples. Such irregularities may not occur in repeated copying under usual condition, but may sometimes occur unfavorably in repeated uses in

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a long term particularly under the environmental conditions of extremely low temperature and low humidity.

Also, under higher temperature and higher humidity conditions, the thickness of the developer layer may sometimes unfavorably change, and become thinner in most cases, thus frequently causing lowering of image density.

As the result of investigations about this point, it has been found that one reason resides in lack of stability and reliability of the charge controller component, and that characteristics of adhesion of the developing powder onto the sleeve and transfer of the developing powder from the sleeve may vary due to change in triboelectric charge.

Explaining in further detail, such irregularities are caused by generation of ununiform portion in amount of triboelectric charges in the developer layer carried on the carrying member due to the change in the environmental conditions. More particularly, under the environmental conditions of extremely low temperature and humidity, a component of the developer with extremely large triboelectric charges is formed through friction of the carrying member surface and the developer. Due to the image force caused by the charges, such a component with extremely large triboelectric charges is liable to be accumulated in

the vicinity of the carrying member and affect influences on evenness or readiness in developing of the upper layer portion of the developer, thereby causing such irregularities as white streaks, spot-like irregularities, and ripple patterns as mentioned  
5 above. The reduction in thickness of the developer layer at higher temperature and humidity may also be generated by uneven triboelectrification between the developer and the carrying member, namely due to  
10 instability of the amount of triboelectric charges of the developer near the surface of the carrying member. As another reason for such an instable amount of triboelectric charges, it may be caused partly because the triboelectrification effect on the developer  
15 particles given by the developer carrying member (sleeve roller), is somewhat weaker than that by the carrier particles in the two-component system developing method.

However, as described previously, the  
20 developer of the present invention has stably a uniform and sharp distribution of the triboelectric charges even under the conditions of higher temperature and humidity or lower temperature and humidity, and therefore it can be a developer most suited for use  
25 in the above developing method.

Next, the developing step according to the process of this invention with the use of the above

developer is described.

Fig. 1 shows a sectional view of one embodiment of the developing system used in the present invention. In the Figure, an electrostatic image bearing member 1 moves in the direction shown by the arrow. A non-magnetic cylinder or sleeve 4 which is a developer carrying member rotates so as to be progressed in the same direction as the movement of the surface of the electrostatic image bearing member at the developing section. Inside the non-magnetic cylinder 4 is provided a multi-polar permanent magnet 9 so as not to be rotated. One-component insulating developer 11 delivered from a developer vessel 12 is coated on the surface of the non-magnetic cylinder 4, and positive charges of opposite polarity to those of the electrostatic image are given to the toner particles. Further, a doctor blade 10 is brought to near the surface of the cylinder (interval  $50\mu$  to  $500\mu$ ) and arranged to confront one magnetic pole (S-pole in the drawing) of the multi-polar permanent magnet 9, whereby the toner layer thickness is evenly regulated thin ( $30\mu$  to  $300\mu$ ). By controlling the rotational speed of the cylinder 4, the surface layer speed and preferably the internal speed of the developer layer are made substantially equal to or approximate to the surface speed of the electrostatic image bearing member 1. As the doctor blade 10, a

permanent magnet may be employed in place of an iron to form a counter-pole. Also, an alternating bias voltage may be applied between the developer carrying member and the electrostatic image bearing surface at the developing section. This alternating bias voltage may have a frequency of 200 to 4000 Hz and Vpp (peak to peak voltage) of 500 to 3000 V.

As described above, in this developing step, for the purpose of having a magnetic developer held stably on a developer carrying member, a non-magnetic cylinder 4 including a multi-polar permanent magnet 9 has been employed. Also, for the purpose of forming the developer layer thin and evenly, a doctor blade 10 made of a magnetic thin plate or a permanent magnet has been arranged in the vicinity of the surface of the cylinder 4. When such a doctor blade of a magnetic material is employed, there is formed a counter-pole against the magnetic pole of the permanent magnet included within the developer carrying member, whereby the toner particle chains are erected forcibly to advantageously regulate the developer layer thin at other portions of the developer carrying member, for example, at the developing position confronting the electrostatic image surface. Further, by giving such a forced movement to the developer, the developer layer can be made more uniform, whereby formation of thin and uniform toner layer not realized by a non-magnetic

doctor blade can be accomplished. Besides, since the gap between the doctor blade and the sleeve can be set relatively wider, an effect of preventing destruction or agglomeration of the toner particles is attained. At the developing station, the toner particles may be transferred through attracting action of the electrostatic image or the action of the alternating bias voltage toward the electrostatic image side.

10           As described above, according to the present invention, there is provided a developer having excellent characteristics as summarized below.

          First, due to the use of fine silica particles treated with a coupling agent as the charge controller and controlled to a hydrophobicity within the range from 30 to 80, particularly when employed as a developer for electrophotography, the amount of triboelectric charges between the toner particles, or the toner and the carrier, or between the toner in case of one-component system developer and a toner carrying member such as a sleeve and the distribution of triboelectric charges are made sharp and even, and thus it is made possible to control the amount of charging to the level suitable for the developing system employed, whereby fogging, and scattering of the toner around edges of the latent image which could not be sufficiently overcome in the prior art, can be

obviated to give a high image density and good reproducibility of half tone.

Further, when the developer is subjected to continuous use over a long term, the characteristics at the initial stage can be maintained and images of high quality can be attained for a long term.

Further, there are important specific features in practical application. One of them is that the distribution of triboelectric charges on the developer under the environmental conditions of higher temperature and humidity is sharp and not substantially changed from that under normal temperature and humidity, and therefore development can be carried out faithfully to the latent image without fog and lowering in image density, and further with excellent transfer efficiency.

Also, even when used under lower temperature and humidity conditions, the distribution of triboelectric charges is not substantially changed, without formation of a developer component with extremely great quantity of charge, and therefore, to be surprising enough, there is neither lowering in image density nor occurrence of fog, substantially without coarsening or scattering of the toner during transfer.

Another specific feature resides in the storage stability that the characteristics at the initial stage can be maintained even after storage for a long term.

Still another specific feature resides in a wide variety of applicable toner compositions because the treated silica of the present invention can be combined with any toner-constituting resins, as contrasted to the pigment or dye of the prior art, which cannot be combined with arbitrary resins but can be combined with only selected binder resins depending on the pigment or dye employed on account of its poor dispersibility. For example, the developer of the invention can be formed into not only a toner of the heat fixation type but also a pressure fixable toner or capsule toner.

Particularly, when the treated fine silica particles are attached on the toner particle surfaces, space charge controlling on the toner surfaces is primarily effected by the fine silica particles, and therefore the above mentioned effects become further marked.

Also, according to the developing method of the present invention by use of the above developer, the triboelectric charges imparted to the developer layer carried on the developer carrying member can be uniformized, permitting excessive charges, which are liable to be generated in successive copying operations under extremely lower temperature and humidity conditions, to be leaked through fine silica particles to an appropriate saturated value, and thus

giving a stable developer layer. Under higher temperature and humidity conditions, the amount of triboelectric charges necessary for giving stable coating conditions can easily be maintained, thus preventing lowering of image density.

Still another specific feature resides in easy formation of a stable developer layer, whereby high image density can be obtained with good reproducibility of half tone, without causing development fog or scattering of the toner around edges of the latent image which has not been overcome in the prior art.

Having described about the basic constitution and specific features of the present invention, the present invention is now specifically described by referring to the following Examples. However, the scope of the present invention are not limited at all by these Examples.

In the following Examples, "parts by weight" and "% by weight" are written merely as "parts" and "%", respectively.

Example 1A

|    |                                      |           |
|----|--------------------------------------|-----------|
|    | Styrene-butyl methacrylate copolymer | 100 parts |
|    | Carbon black                         | 2 parts   |
| 25 | Nigrosine                            | 3 parts   |

The above materials were sufficiently blended in a blender and then kneaded on a twin roll heated to

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150°C. The kneaded product was left to cool, coarsely crushed by a cutter mill, pulverized by means of a micropulverizer with a jet air stream and further subjected to classification by use of a wind force classifier to obtain colored fine powder with particle sizes of 5 to 20 $\mu$ .

As the next step, fine silica particles Aerosil 200 (produced by Nippon Aerosil Co.) were placed in a sealed type Henschel mixer heated to 70°C and stirred at a high speed, while adding to the silica dropwise  $\gamma$ -aminopropyl triethoxysilane diluted with alcohol to a treated quantity of 2.0% of the silane coupling agent based on the silica. The fine particles obtained were dried at 120°C and thereafter placed into a Henschel mixer, and dimethyl dichlorosilane was added to the silica under stirring to a content of 2.0%. The mixture was subjected to a high speed stirring at room temperature for 2 hours, followed further by stirring at 80°C for 24 hours, and then the mixer was opened to atmospheric pressure. This mixture was dried at atmospheric pressure under further stirring at a low speed at 60°C for 5 hours. The treated fine silica particles obtained (positive charge controller) had a hydrophobicity of 50, a mean primary particle size of 12 m $\mu$ , and a mean secondary particle size of 0.2 $\mu$ .

To 5 parts of a mixture of the above colored

fine powder and 0.6% of the treated fine silica particles added and mixed therewith by a Henshcel mixer, 100 parts of iron powder carrier with particle sizes of 50 to 80 $\mu$  were added and mixed to prepare a  
5 developer.

Then, according to the electrophotographic method of the prior art, negative electrostatic images were formed on an OPC sensitive material (resinous laminar coating layers containing a phthalocyanin  
10 pigment and a hydrazone compound, respectively) by subjecting it to corona-discharging at -6KV and irradiation with original image light and subjected to powder development according to a conventional  
two-component magnetic brush method with the use of  
15 the above developer to form toner images, which were in turn transferred onto plain paper and fixed by heating. The transferred images obtained were found to be good with high resolution, having sufficiently high densities up to 1.5, without fog at all, being  
20 also free from scattering of the toner around the images. Transferred images were formed continuously by use of the above developer for examination of its performances under successive copying operations to give the result that the transferred image after  
25 copying 30000 sheets was found to be totally comparable to the images at the initial stage.

When the environmental conditions were

changed to 35°C and 85% R.H., the image density was 1.39, which was a value substantially unchanged from that under normal temperature and normal humidity (i.e. 22°C, 60% R.H.) conditions, and clear images could be obtained without fog and scattering of the toner, indicating substantially the same performances up to 30000 sheets of copying. Then, when transferred images were obtained at a low temperature and a low humidity of 10°C and 10%, the image densities were found to be high up to 1.60, and the solid black portions could be developed and transferred very smoothly to give excellent images without scattering or drop-off of the toner. When successive copying was conducted under these environmental conditions, both continuously and intermittently, the density fluctuation was within  $\pm 0.2$  up to 30000 sheets of copying, thus showing that the developer was satisfactory in practical applications.

The results of measurements of the distributions in amount of triboelectric charges on this developer are shown in Fig. 2(a) through (c), which indicate sharp distributions under respective conditions of normal temperature, normal humidity; high temperature, high humidity; and low temperature, low humidity.

#### Comparative Example 1A

A developer was prepared in the same manner

as in Example 1A, except that Aerosil 200 was not treated with  $\gamma$ -aminopropyltriethoxysilane nor with dimethyldichlorosilane, and development and transfer were also conducted similarly. As the result, only  
5 reversed images could be obtained, and the amount of triboelectric charges was  $-3.2 \mu\text{C/g}$ , exhibiting a negative charging characteristic.

Comparative Example 2A

A developer was prepared in the same manner  
10 as in Example 1A except that no treatment with dimethyldichlorosilane was applied, and images were obtained similarly. At normal temperature and normal humidity, fog occurred little, but the image density was as low as 0.84 with conspicuous coarsening at the  
15 solid black portions. When successive copying test was conducted, the density was lowered to 0.46 on copying of 2000 sheets. When images were obtained under the conditions of  $35^{\circ}\text{C}$  and 85%, the image density was lowered to 0.50 with increase of fog, scattering  
20 of the toner and coarsening of the image, proving to be practically unuseful. The transfer efficiency was also as low as 63%.

When the images were obtained under the conditions of  $10^{\circ}\text{C}$  and 10% R.H., the image density  
25 was as low as 0.70, with excessive scattering, fog and coarsening, and transfer drop-off was markedly observed. Continuous image formation was effected

until about 500 copies were produced, when the density became 0.40 to make copying no longer practically possible. The results of measurements of the triboelectric charge distributions on this developer are shown by the full lines in Fig. 3(a) through (c).

As described above, its distribution was broad in any environment, evidencing a large content of components having deleterious effects on development and transfer.

Examples 2A - 5A

10                   When Example 1A was repeated except that the amounts of  $\gamma$ -aminopropyl triethoxysilane and dimethyldichlorosilane treated on Aerosil 200 were changed to 0.5%, 1.0%; 2.0%, 5.0%; 10.0%, 5.0%; and 10.0%, 10.0%, respectively, good results could be  
15                   obtained.

Example 6A

|    |                                           |           |
|----|-------------------------------------------|-----------|
|    | Styrene-butyl methacrylate copolymer      | 100 parts |
|    | Carbon black                              | 2 parts   |
|    | Nigrosine                                 | 3 parts   |
| 20 | Fine silica powders prepared in Example 1 | 10 parts  |

                  The above components were kneaded, pulverized and classified to obtain fine powder with particle sizes of 5 to 20 $\mu$ , and further the silica particles prepared in Example 1A were added to and mixed with  
25                   the above fine powder in an amount of 0.3% based on said fine powder. Otherwise, the procedure of Example

1A was substantially followed to obtain good results.

Example 7A

Substantially the same procedure as in Example 1A was repeated except that N,N-dimethylamino-phenyl triethoxysilane was employed in place of  $\gamma$ -aminopropyl triethoxysilane, whereby good results were obtained.

Example 8A

Substantially the same procedure as in Example 1A was repeated except that aminoethylamino-methylphenethyl triethoxysilane was employed in place of  $\gamma$ -aminopropyl triethoxysilane, whereby good results were obtained.

Example 9A

|    |              |           |
|----|--------------|-----------|
| 15 | Polyethylene | 100 parts |
|    | Carbon black | 1 part    |
|    | Spirit black | 2 parts   |

Except for preparing a toner from the above materials according to the method as described in

20 Example 1A, the same procedure as in Example 1A was followed to give good results.

Evaluations of respective Examples and Comparative Examples mentioned above are shown in Table 1.

Table 1-1

|                           | Normal Temperature, Normal Humidity |          |                 |                 |                                       |                                                                    |                       |
|---------------------------|-------------------------------------|----------|-----------------|-----------------|---------------------------------------|--------------------------------------------------------------------|-----------------------|
|                           | Image density                       | Fog      | Scatter-<br>ing | Resolu-<br>tion | Density on<br>copying<br>30000 sheets | Average amount<br>of triboelec-<br>tric charges<br>$\mu\text{C/g}$ | Standard<br>deviation |
| Example 1A                | 1.50                                | good     | good            | good            | 1.39                                  | + 11.0                                                             | 2.9                   |
| 2A                        | 1.32                                | good     | good            | good            | 1.30                                  | + 5.2                                                              | 3.4                   |
| 3A                        | 1.46                                | good     | good            | good            | 1.40                                  | + 7.4                                                              | 3.1                   |
| 4A                        | 1.35                                | good     | good            | good            | 1.30                                  | + 10.5                                                             | 2.7                   |
| 5A                        | 1.41                                | good     | good            | good            | 1.31                                  | + 8.7                                                              | 3.0                   |
| 6A                        | 1.29                                | good     | good            | good            | 1.25                                  | + 7.2                                                              | 2.4                   |
| 7A                        | 1.41                                | good     | good            | good            | 1.35                                  | + 7.6                                                              | 2.5                   |
| 8A                        | 1.36                                | good     | good            | good            | 1.30                                  | + 9.1                                                              | 3.0                   |
| Comparative<br>Example 1A | 0.07                                | reversed | bad             | bad             | -                                     | - 3.2                                                              | 7.0                   |
| 2A                        | 0.84                                | bad      | bad             | bad             | on copying<br>2000 sheets<br>0.46     | + 15.0                                                             | 11.0                  |

Table 1-2

|                        | 35°C 85%          |                         |                                 |                                                         |                    |
|------------------------|-------------------|-------------------------|---------------------------------|---------------------------------------------------------|--------------------|
|                        | Image density     | Transfer efficiency (%) | Density on copying 30000 sheets | Average amount of triboelectric charges $\mu\text{C/g}$ | Standard deviation |
| Example 1A             | 1.39              | 89                      | 1.30                            | + 8.0                                                   | 3.4                |
| 2A                     | 1.27              | 87                      | 1.30                            | + 4.8                                                   | 3.6                |
| 3A                     | 1.31              | 87                      | 1.35                            | + 6.1                                                   | 3.1                |
| 4A                     | 1.20              | 87                      | 1.25                            | + 8.4                                                   | 3.7                |
| 5A                     | 1.20              | 89                      | 1.28                            | + 6.7                                                   | 3.4                |
| 6A                     | 1.20              | 90                      | 1.29                            | + 6.2                                                   | 3.4                |
| 7A                     | 1.35              | 93                      | 1.35                            | + 6.8                                                   | 3.0                |
| 8A                     | 1.28              | 90                      | 1.26                            | + 8.5                                                   | 3.2                |
| Comparative Example 1A | No image obtained | -                       | -                               | - 0.5                                                   | 5.5                |
| 2A                     | 0.50              | 63                      | 0.20                            | + 2.7                                                   | 8.5                |

Table 1-3

|                        | 10°C 10%      |                         |                                 |                                                         |                    | Hydro-phobicity of silica |
|------------------------|---------------|-------------------------|---------------------------------|---------------------------------------------------------|--------------------|---------------------------|
|                        | Image density | Transfer efficiency (%) | Density on copying 30000 sheets | Average amount of triboelectric charges $\mu\text{c/g}$ | Standard deviation |                           |
| Example 1A             | 1.60          | 92                      | 1.40                            | + 12.0                                                  | 3.2                | 50                        |
| 2A                     | 1.20          | 90                      | 1.35                            | + 5.9                                                   | 3.5                | 35                        |
| 3A                     | 1.39          | 87                      | 1.36                            | + 7.6                                                   | 3.5                | 60                        |
| 4A                     | 1.20          | 86                      | 1.31                            | + 11.2                                                  | 3.2                | 60                        |
| 5A                     | 1.45          | 88                      | 1.40                            | + 9.0                                                   | 3.2                | 80                        |
| 6A                     | 1.35          | 91                      | 1.40                            | + 7.5                                                   | 3.0                | 50                        |
| 7A                     | 1.32          | 90                      | 1.35                            | + 8.0                                                   | 3.0                | 70                        |
| 8A                     | 1.32          | 90                      | 1.35                            | + 9.5                                                   | 3.4                | 70                        |
| Comparative Example 1A | 0.05          | 35                      | 0.12                            | - 11.0                                                  | 10.3               | 0                         |
| 2A                     | 0.70          | 70                      | On copying 500 sheets 0.40      | + 26.0                                                  | 21.0               | 0                         |

(82)

Example 1B

In Example 1A, fine silica particles Aerosil 200 were subjected to the heat treatment at 800°C for one hour and otherwise the same procedure as in  
5 Example 1A was followed to obtain treated fine silica particles with a hydrophobicity of 55.

With the use of the treated fine silica particles similarly as in Example 1A, a developer was prepared, and development of negative electrostatic  
10 images according to the magnetic brush method and transfer onto plain paper were performed. The image densities obtained under various conditions are shown below. The developer characteristics including the results of successive copying tests were equal to or  
15 better than those obtained in Example 1A.

|                |      |
|----------------|------|
| 22°C, 60% R.H. | 1.53 |
|----------------|------|

|                |      |
|----------------|------|
| 35°C, 85% R.H. | 1.50 |
|----------------|------|

|                |      |
|----------------|------|
| 10°C, 10% R.H. | 1.50 |
|----------------|------|

Also, as the test for examination of storage  
20 stability, the developer was stored under the conditions of 35°C, 90% R.H. for one month, and even after the storage test, the image obtained was clear substantially without lowering of image density as compared with that before storage.

25 The results of measurement of the distributions of triboelectric charges on this developer are shown in Fig. 4(a) through (c), which exhibit further

sharper distributions than those in Example 1A under the respective conditions of normal temperature and normal humidity, higher temperature and higher humidity, and lower temperature and lower humidity.

5. Comparative Example 1B

A developer was prepared in the same manner as in Example 1B, except that Aerosil 200 was not treated with  $\gamma$ -aminopropyltriethoxysilane and dimethyldichlorosilane, and development and transfer were also conducted similarly. The results obtained were unsatisfactory, similarly as in Comparative Example 1A.

Comparative Example 2B

A developer was prepared in the same manner as in Example 1B except that no treatment with dimethyldichlorosilane was applied, and images were obtained similarly. The results obtained were unsatisfactory, similarly as in Comparative Example 2A.

Examples 2B - 9B

When Example 1B was repeated except that the heat treatment temperatures were changed to 430°C, 480°C, 500°C, 600°C, 700°C, 900°C, 1000°C, 1200°C, respectively, good results could be obtained.

Example 10B

When Example 1B was repeated except that the amounts of  $\gamma$ -aminopropyltriethoxysilane and dimethyldichlorosilane treated on Aerosil 200 were changed to

10% and 5.0%, respectively, good results could be obtained.

Example 11B

|   |              |           |
|---|--------------|-----------|
| 5 | Polyethylene | 100 parts |
|   | Carbon black | 1 part    |
|   | Spirit black | 2 parts   |

The above materials were made into a toner according to the same procedure as in Example 1B, following otherwise the same procedure as in Example 10 1B. As the result, good results could be obtained.

The results of evaluation of Examples 1B to 11B are summarized in Table 2 together with those of Comparative Examples 1B and 2B.

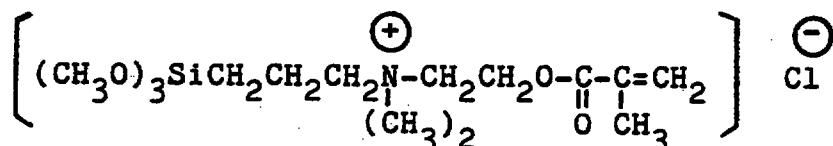
Table 2

|                           | Before storage   |                                                            |                       | After stored at 35°C,<br>90% R.H., for one month |                                                            |                       | Hydro-<br>phobi-<br>city of<br>silica |
|---------------------------|------------------|------------------------------------------------------------|-----------------------|--------------------------------------------------|------------------------------------------------------------|-----------------------|---------------------------------------|
|                           | Image<br>density | Amount of<br>triboelec-<br>tric charges<br>$\mu\text{c/g}$ | Standard<br>deviation | Image<br>density                                 | Amount of<br>triboelec-<br>tric charges<br>$\mu\text{c/g}$ | Standard<br>deviation |                                       |
| Example 1B                | 1.53             | + 11.5                                                     | 2.5                   | 1.50                                             | + 10.5                                                     | 2.9                   | 55                                    |
| 2B                        | 1.40             | + 8.5                                                      | 3.4                   | 1.35                                             | + 8.3                                                      | 3.5                   | 50                                    |
| 3B                        | 1.42             | + 9.1                                                      | 3.4                   | 1.38                                             | + 9.0                                                      | 3.5                   | 50                                    |
| 4B                        | 1.38             | + 9.0                                                      | 3.3                   | 1.36                                             | + 8.5                                                      | 3.9                   | 55                                    |
| 5B                        | 1.50             | + 9.5                                                      | 3.0                   | 1.45                                             | + 9.3                                                      | 3.5                   | 58                                    |
| 6B                        | 1.47             | + 9.6                                                      | 2.9                   | 1.47                                             | + 9.5                                                      | 3.3                   | 55                                    |
| 7B                        | 1.47             | + 9.6                                                      | 3.4                   | 1.47                                             | + 9.2                                                      | 3.2                   | 55                                    |
| 8B                        | 1.40             | + 9.9                                                      | 3.1                   | 1.35                                             | + 9.7                                                      | 3.0                   | 60                                    |
| 9B                        | 1.42             | + 8.2                                                      | 3.2                   | 1.42                                             | + 8.0                                                      | 3.8                   | 60                                    |
| 10B                       | 1.52             | + 7.5                                                      | 2.5                   | 1.50                                             | + 7.5                                                      | 2.8                   | 75                                    |
| 11B                       | 1.27             | + 9.2                                                      | 2.8                   | 1.19                                             | + 9.0                                                      | 3.6                   | 55                                    |
| Comparative<br>Example 1B | 0.07             | - 3.2                                                      | 7.0                   | No image<br>obtained                             | - 1.0                                                      | 6.5                   | 0                                     |
| 2B                        | 0.84             | + 15.0                                                     | 11.0                  | 0.60                                             | + 3.3                                                      | 7.2                   | 0                                     |

Example 1C

|   |                                     |       |
|---|-------------------------------------|-------|
|   | 3-Chloropropyl trimethoxysilane     | 50 g  |
|   | Methyl iodide                       | 0.5 g |
|   | 2-(Dimethylamino)ethyl methacrylate | 50 g  |
| 5 | Dimethylformamide                   | 100 g |
|   | Sulfur                              | 0.5 g |

The above mixture was allowed to react under reflux at 90°C for 50 hours to obtain a product:



10        Next 100g of fine silica particles Aerosil 200  
 (produced by Nippon Aerosil Co) were immersed in an  
 aqueous solution having diluted 2g of the above  
 product, and the mixture was stirred at 60°C for one  
 hour. Then, the mixture was filtered and dried at  
 15    100°C for 10 hours to obtain fine silica particles  
 treated with a cation type unsaturated amine. The  
 silica was placed into a Henschel mixer, and dimethyl-  
 dichlorosilane was sprayed onto the silica under  
 stirring to a quantity of 5%. High speed stirring was  
 20    continued at room temperature for 2 hours, and the  
 mixture was further stirred at 80°C for 24 hours,  
 followed by opening of the mixer to atmospheric  
 pressure. The mixture was further subjected to drying  
 at low speed under atmospheric pressure at 60°C for 5  
 25    hours. The thus prepared treated silica had a hydro-  
 phobicity of 60.

Styrene-butadiene copolymer (70:30) 100 parts  
Carbon black 2 parts  
Nigrosine 3 parts

As the next step, the above materials were  
5 sufficiently blended in a blender and then kneaded  
on a twin roll heated to 150°C. The kneaded product  
was left to cool, coarsely crushed by a cutter mill, -  
pulverized by means of a micropulverizer with a jet  
air stream and further subjected to classification  
10 by use of a wind force classifier to obtain colored  
fine powder of 5 to 20 $\mu$ .

A developer was prepared by adding 100 parts  
of iron powder carrier with particle sizes of 50 to  
80 $\mu$  to 5 parts of a mixture prepared by adding 0.6%  
15 of the above treated silica to the colored fine  
powder.

With the use of this developer, following  
otherwise the same procedure as in Example 1A, develop-  
ment of the negative electrostatic images according  
20 to the magnetic brush method and transfer onto plain  
paper were performed. The image densities obtained  
under various conditions are shown below. The  
developer characteristics including the results of  
successive copying tests were found to be substan-  
25 tially as good as those obtained in Example 1A.

22°C, 60% R.H. 1.31

35°C, 85% R.H. 1.25

10°C, 10% R.H. 1.35

Comparative Example 1C

A developer was prepared in the same manner as in Example 1C, except that Aerosil 200 was not  
5 treated with the compound prepared in Example 1C and dimethyldichlorosilane, and development and transfer were also conducted similarly. As the result, only - reversed images could be obtained, and the amount of triboelectric charges was  $-2.8 \mu\text{c/g}$ , exhibiting a  
10 negative charging characteristic.

Comparative Example 2C

A developer was prepared in the same manner as in Example 1C except that no treatment with dimethyldichlorosilane was applied, and images were  
15 obtained similarly. At normal temperature and normal humidity, fog and scattering occurred frequently, and the image density was as low as 0.65. Also, the image exhibited coarsening tendency, proving to be practically unuseful.

20 Examples 2C - 4C

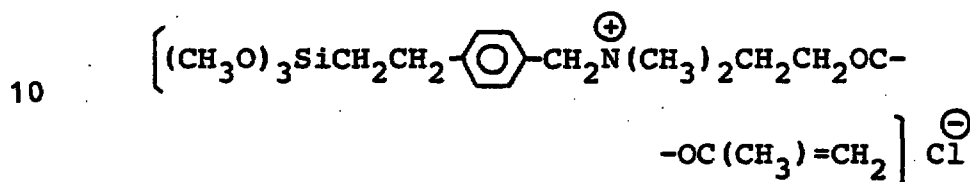
When Example 1C was repeated under substantially the same conditions except that the amounts of the compound prepared in Example 1C and dimethyldichlorosilane treated on Aerosil 200 were changed to  
25 0.3%, 1.0%; 1.0%, 1.0%; and 5.0%, 1.0%, respectively, good results could be obtained.

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Example 5C

|   |                                                                                             |       |
|---|---------------------------------------------------------------------------------------------|-------|
|   | $\text{CH}_2=\text{C}(\text{CH}_3)\text{COOCH}_2\text{CH}_2-\text{N}(\text{CH}_3)_2$        | 4 g   |
|   | $(\text{CH}_3\text{O})_3\text{SiCH}_2\text{CH}_2-\text{C}_6\text{H}_4-\text{CH}_2\text{Cl}$ | 5 g   |
|   | Methyliodide                                                                                | 0.5 g |
| 5 | t-Butyl alcohol                                                                             | 50 g  |
|   | Sulfur                                                                                      | 0.3 g |

The above mixture was refluxed at 100°C for one hour to obtain a product:



Subsequently, fine silica particles of Aerosil 200 were mixed in a Henschel mixer with the above product by spraying an aqueous solution thereof to a content of 5%. Then, the mixture was dried at 100°C for 10 hours to obtain fine silica particles treated with a cation type unsaturated amine. The silica was again thrown into a Henschel mixer, and dimethyldichlorosilane was sprayed onto said silica under stirring to a quantity of 2%. Then, the same treatments as in Example 1C were applied. The hydrophobicity was found to be 50.

|    |                    |           |
|----|--------------------|-----------|
|    | Polyethylene oxide | 100 parts |
|    | Carbon black       | 3 parts   |
| 25 | Nigrosine          | 3 parts   |

With the use of the above materials, the same procedure as described in Example 1C was repeated

to obtain fine powder of 5 to 25 $\mu$ . A developer was prepared by adding 100 parts of iron powder carrier of particle sizes of 100 to 200 $\mu$  to 10 parts of a mixture prepared by adding 0.3% of the above treated silica to the fine powder.

Next, images were obtained similarly as in Example 1C, followed by pressure fixing. The image density was found to be sufficiently high up to 1.53, and also faithful to the latent image. As the result of successive copying tests, the images obtained were practically satisfactory until copying of 20000 sheets, and excellent characteristics were exhibited under higher temperature and higher humidity conditions of 35°C and 85% R.H., as well as under lower temperature and lower humidity conditions of 10°C and 10% R.H.

Evaluations of Examples 1C - 5C and Comparative Examples 1C and 2C are listed in Table 3.

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Table 3-1

|                           | Normal Temperature, Normal Humidity |                                    |               |                 |                 | 35°C 85%      |                                    |                             |
|---------------------------|-------------------------------------|------------------------------------|---------------|-----------------|-----------------|---------------|------------------------------------|-----------------------------|
|                           | Image density                       | Density on copying<br>30000 sheets | Fog           | Scatter-<br>ing | Resolu-<br>tion | Image density | Density on copying<br>30000 sheets | Transfer effi-<br>cency (%) |
| Example 1C                | 1.31                                | 1.20                               | Good          | Good            | Good            | 1.25          | 1.16                               | 83                          |
| 2C                        | 1.22                                | 1.18                               | Good          | Good            | Good            | 1.15          | 1.24                               | 85                          |
| 3C                        | 1.26                                | 1.28                               | Good          | Good            | Good            | 1.18          | 1.16                               | 88                          |
| 4C                        | 1.35                                | 1.28                               | Good          | Good            | Good            | 1.21          | 1.12                               | 85                          |
| 5C                        | 1.53                                | On copying<br>20000<br>sheets 1.20 | Good          | Good            | Good            | 1.30          | On copying<br>20000<br>sheets 1.10 | 88                          |
| Comparative<br>Example 1C | Re-<br>versed                       | -                                  | Re-<br>versed | Bad             | Bad             | No<br>image   | -                                  | -                           |
| 2C                        | 0.65                                | On copying<br>1000<br>sheets 0.30  | Bad           | Bad             | Bad             | 0.42          | -                                  | 60                          |

Table 3-2

|                        | 10°C 10%      |                                       |                         | Hydrophobicity of silica |
|------------------------|---------------|---------------------------------------|-------------------------|--------------------------|
|                        | Image density | Image density on copying 30000 sheets | Transfer efficiency (%) |                          |
| Example 1C             | 1.35          | 1.28                                  | 90                      | 60                       |
| 2C                     | 1.25          | 1.25                                  | 88                      | 62                       |
| 3C                     | 1.30          | 1.34                                  | 90                      | 60                       |
| 4C                     | 1.27          | 1.17                                  | 90                      | 60                       |
| 5C                     | 1.32          | On copying 20000 sheets 1.10          | 92                      | 50                       |
| Comparative Example 1C | Reversed      | -                                     | -                       | 0                        |
| 2C                     | 0.31          | -                                     | 60                      | 0                        |

Example 1D

|                                      |           |
|--------------------------------------|-----------|
| Styrene-butyl methacrylate copolymer | 100 parts |
| Carbon black                         | 2 parts   |
| Nigrosine                            | 3 parts   |

5           The above materials were well blended in  
a blender and then kneaded on a twin roll heated to  
150°C. The kneaded product was left to cool, coarsely  
crushed by a cutter mill, pulverized by means of a  
micropulverizer with a jet air stream and further  
10 subjected to classification by use of a wind force  
classifier to obtain colored fine powder of 5 to 20 $\mu$ .

As the next step, fine silica particles  
Aerosil 200 (produced by Nippon Aerosil Co.) were  
placed in a sealed type Henschel mixer heated to 70°C  
15 and stirred at a high speed, while adding to the  
silica dropwise  $\gamma$ -aminopropyl triethoxysilane diluted  
with alcohol to a treated quantity of 5.0% of the  
silane coupling agent based on silica. The fine  
particles obtained were dried at 120°C and thereafter  
20 placed again into a Henschel mixer, and dimethyl  
silicone oil (viscosity: 100 centipoise at 25°C) was  
added to the silica under stirring to a quantity of  
2.0%. The mixture was subjected to a high speed  
stirring at room temperature for 2 hours, followed  
25 further by stirring continued at 160°C for 15 hours,  
and then the mixer was opened to atmospheric pressure.  
This mixture was further dried at room temperature

under atmospheric pressure for 5 hours. The degree of hydrophobicity was found to be 70.

To 10 parts of a mixture of 0.4% of the treated fine silica particles added to and mixed with the aforesaid fine powder by a Henschel mixer, 100 parts of iron powder carrier with particle sizes of 100 to 130 $\mu$  were added to prepare a developer.

With the use of this developer, following otherwise the same procedure as in Example 1A, development of the negative electrostatic images according to the magnetic brush method and transfer onto plain paper were performed. The image densities obtained under various conditions are shown below. The developer characteristics were substantially comparable to those obtained in Example 1A.

|                |      |
|----------------|------|
| 22°C, 60% R.H. | 1.4  |
| 35°C, 85% R.H. | 1.30 |
| 10°C, 10% R.H. | 1.45 |

In successive copying tests, no abnormality was observed until 100,000 sheets of copying, and the density fluctuation was practically satisfactory within  $\pm 0.3$ .

#### Comparative Example 1D

A developer was prepared in the same manner as in Example 1D, except that Aerosil 200 was not treated with  $\gamma$ -aminopropyltriethoxysilane and dimethyl silicone oil, and development and transfer were also

conducted similarly. As the result, only reversed images could be obtained, and the amount of tribo-electric charges was  $-3.2 \mu\text{c/g}$ , exhibiting a negative charging characteristic. The hydrophobicity of silica was found to be 0.

Comparative Example 2D

A developer was prepared in the same manner as in Example 1D except no treatment with dimethyl silicon oil was applied, and images were obtained similarly. At normal temperature and normal humidity, fog occurred little, but the image density was as low as 0.84 with conspicuous coarsening at the solid black portions. When successive copying test was conducted, the density was lowered to 0.46 on copying of 2000 sheets, and image flow occurred on copying 3000 sheets. When images were obtained under the conditions of  $35^{\circ}\text{C}$  and 85%, the image density was lowered to 0.50 with increase of fog, scattering of the toner and coarsening of the image, thus being practically useless. The transfer efficiency was also as low as 63%. The hydrophobicity of silica was 0.

When images were obtained under the conditions of  $10^{\circ}\text{C}$  and 10% R.H., the image density was as low as 0.70, with excessive scattering, fog and coarsening, and transfer drop-off was markedly observed. Continuous image formation was effected

until about 500 copies were obtained, when the density became 0.40 to make copying no longer practically possible.

Example 2D

5                    Example 1D was repeated except for using methyl hydrogen silicone oil (trade name: TSF 484, produced by Toshiba Silicone Co.) in place of dimethyl silicone oil, whereby good results were obtained.

Example 3D

|    |              |           |
|----|--------------|-----------|
| 10 | Polyethylene | 100 parts |
|    | Carbon black | 1 part    |
|    | Spirit black | 2 parts   |

15                    The above materials were made into a toner according to the same procedure as in Example 1D, following otherwise the same procedure as in Example 1D. As the result, good results could be obtained.

Example 4D

20                    The experiment was conducted in substantially the same manner as in Example 1D except for replacing  $\gamma$ -aminopropyltriethoxysilane with N,N-dimethylamino-phenyl triethoxysilane to obtain good results. The hydrophobicity of silane was 75. The results of evaluation of Examples 1D to 4D are summarized in Table 4 together with those of Comparative Examples 1D and 2D.

25

Table 4-1

|                        | Normal Temperature, Normal Humidity |                                  |      |             |             | 35°C 85%      |                                  |                          |                                         |
|------------------------|-------------------------------------|----------------------------------|------|-------------|-------------|---------------|----------------------------------|--------------------------|-----------------------------------------|
|                        | Image density                       | Density on copying 100000 sheets | Fog  | Scat-tering | Reso-lution | Image density | Density on copying 100000 sheets | Transfer effici-ency (%) | Image flow                              |
| Example 1D             | 1.40                                | 1.31                             | Good | Good        | Good        | 1.30          | 1.26                             | 92                       | Good                                    |
| 2D                     | 1.33                                | 1.30                             | Good | Good        | Good        | 1.18          | 1.24                             | 90                       | Good                                    |
| 3D                     | 1.60                                | 1.40                             | Good | Good        | Good        | 1.41          | 1.36                             | 90                       | Good                                    |
| 4D                     | 1.36                                | 1.30                             | Good | Good        | Good        | 1.25          | 1.20                             | 92                       | Good                                    |
| Comparative Example 1D | Re-versed                           | -                                | Bad  | Bad         | Bad         | No image      | -                                | -                        | -                                       |
| 2D                     | 0.84                                | -                                | Fair | Bad         | Bad         | 0.50          | -                                | 63                       | Bad generated on copying of 3000 sheets |

Table 4-2

|                        | After storage for one month at 35°C, 90%R.H. |      |             |             |               | 10°C 10%                         |                   |             |  |
|------------------------|----------------------------------------------|------|-------------|-------------|---------------|----------------------------------|-------------------|-------------|--|
|                        | Image density                                | Fog  | Scat-tering | Reso-lution | Image density | Density on copying 100000 sheets | Transfer drop-off | Scatter-ing |  |
| Example 1D             | 1.30                                         | Good | Good        | Good        | 1.35          | 1.15                             | Good              | Good        |  |
| 2D                     | 1.26                                         | Good | Good        | Good        | 1.35          | 1.24                             | Good              | Good        |  |
| 3D                     | 1.42                                         | Good | Good        | Good        | 1.60          | 1.43                             | Good              | Good        |  |
| 4D                     | 1.30                                         | Good | Good        | Good        | 1.35          | 1.28                             | Good              | Good        |  |
| Comparative Example 1D | Pale reversed image                          | Bad  | Bad         | Bad         | Reversed      | -                                | -                 | -           |  |
| 2D                     | 0.58                                         | Bad  | Bad         | Bad         | 0.70          | -<br>On copying 500 sheets 0.40  | Fair              | Bad         |  |

Example 1E

|                                     |           |
|-------------------------------------|-----------|
| Styrene-butadiene copolymer (70:30) | 100 parts |
| Carbon black                        | 3 parts   |
| Nigrosine                           | 4 parts   |

5           The above materials were well blended in  
a blender and then kneaded on a twin roll heated to  
150°C. The kneaded produce was left to cool, coarsely  
crushed by a cutter mill, pulverized by means of a  
micropulverizer with a jet air stream and further  
10 subjected to classification by use of a wind force  
classifier to obtain colored fine powder of 5 to 20 $\mu$ .

As the next step, fine silica particles  
Aerosil 200 (produced by Nippon Aerosil Co.) were  
placed in a sealed type Henschel mixer heated to  
15 70°C and stirred at a high speed, while adding to  
the silica dropwise isopropyl tri-isostearoyl titanate  
diluted with alcohol to a treated quantity of 2.0% of  
the titanium coupling agent based on the silica. The  
fine particles obtained were dried at 120°C.

20           A developer was prepared by adding 100 parts  
of iron powder carrier with particle sizes of 50 to  
80 $\mu$  to 5 parts of a mixture prepared by adding 0.6%  
of the treated silica to the above fine powder. The  
amount of triboelectric charges was as high as  
25 +18.6  $\mu$ c/g.

With the use of this developer, following  
otherwise the same procedure as in Example 1A,

development of the negative electrostatic images according to the magnetic brush method and transfer onto plain paper were performed. The image densities obtained under various conditions are shown below.

- 5 The developer characteristics were substantially comparable to those obtained in Example 1A.

|                |      |
|----------------|------|
| 22°C, 60% R.H. | 1.5  |
| 35°C, 85% R.H. | 1.42 |
| 10°C, 10% R.H. | 1.40 |

- 10 In successive copying tests, no abnormality was observed until 100,000 sheets of copying, and the density fluctuation was practically satisfactory within  $\pm 0.2$ .

- After this developer was stored under an  
15 environment of 35°C and 90% R.H. for one month, images were also obtained by use of this developer, whereby the image density was substantially unchanged as 1.38 and the image quality was also good.

Comparative Example 1E

- 20 A developer was prepared in the same manner as in Example 1E, except that Aerosil 200 was not treated with isopropyl tri-isostearoyl titanate, and development and transfer were also conducted similarly. As the result, only reversed images could be obtained,  
25 and the amount of triboelectric charges was  $-3.0 \mu\text{c/g}$ , exhibiting a negative charging characteristic.

Example 2E

Example 1E was repeated except for replacing isopropyl tri-stearoyl titanate with isopropyl tri(N, N-dimethylethylamino)titanate, whereby there were  
5 obtained images of a high density of 1.31 which are faithful to latent images having high resolution without fog, scattering or transfer drop-off.

After successive copying tests of 100,000 sheets, the images obtained were comparable to those  
10 at the initial stage. After storage under an environment of 35°C and 90% R.H. for one month, this developer was employed for image formation to give the result that the image density was 1.30 as before, and the image quality was also good. When image formation  
15 was effected at 35°C, 85% R.H., very good images could be obtained from the initial stage, and the images after 100,000 sheets of copying were also good. The transfer efficiency was also excellent and as high as 92%.

20 Example 3E

Example 1E was repeated except that di-anthranylethylene titanate was used for treating in an amount of 10% on the silica in place of isopropyl tri-stearoyl titanate. The resultant developer  
25 exhibited excellent image quality and durability under respective environments of lower temperature and lower humidity, higher temperature and higher

humidity, and normal temperature and normal humidity.

Example 1F

A mixture of 100 parts of zinc oxide, 20 parts of styrene-butadiene copolymer, 40 parts of  
5 n-butyl methacrylate, 120 parts of toluene and 4 parts of 1% Rose Bengal solution in methanol was dispersed by mixing in a ball mill for 6 hours. This dispersion was applied as a coating by a wire bar on an aluminum plate of 0.05 mm thickness in an amount to give a  
10 dry coating thickness of 40 $\mu$ , followed by evaporation of the solvent by hot air to prepare a zinc oxide-binder type photosensitive material, which was then formed into a shape of drum. This photosensitive material was subjected to corona discharging at -6KV  
15 to be charged evenly over all the surface, and thereafter an original image irradiation was effected to form an electrostatic latent image.

A developer carrying member in the form of a cylindrical sleeve of stainless steel with an  
20 outer diameter of 50 mm was used. A magnetic flux density on the sleeve surface of 700 Gauss was applied, and a distance between the doctor blade and the sleeve surface was set at 0.2 mm. A rotary sleeve fixed magnet type developing device was set at a  
25 distance of 0.25 mm between the aforesaid photosensitive drum surface and the sleeve surface (the circumferential velocity of the sleeve being the same

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as that of the drum, with rotational directions opposite to each other), and an alternating voltage of 400 Hz, 1000 V and a direct bias voltage of -150 V were applied on the sleeve.

5                   One hundred (100) parts of Priorite S-5A (styrene-butadiene copolymer, produced by Goodyear Chemicals), 60 parts of magnetite and 3 parts of nigrosine spirit were mixed well in a blender and then kneaded on a twin roll heated to 150°C. The  
10 kneaded product was left to cool, coarsely crushed by a cutter mill, pulverized by means of a micro-pulverizer with a jet air stream and further subjected to classification by use of a wind force classifier to obtain colored fine powder of 5 to 20 $\mu$ .

15                   As the next step, fine silica particles Aerosil 200 (produced by Nippon Aerosil Co.) were placed in a sealed type Henschel mixer heated to 70°C and stirred at a high speed, while adding to the silica dropwise  $\gamma$ -aminopropyl triethoxysilane diluted with  
20 alcohol to a treated quantity of 10% of the silane coupling agent based on the silica. The fine particles obtained were dried at 120°C and thereafter placed again into a Henschel mixer, and dimethyl dichloro-silane was sprayed onto the silica under stirring to  
25 a content of 10%. The mixture was subjected to a high speed stirring at room temperature for 2 hours, followed further by stirring continued at 80°C for

24 hours, and then the mixer was opened to atmospheric pressure. This mixture was dried at atmospheric pressure under further stirring at a low speed at 60°C for 5 hours. The hydrophobicity of the treated silica was 60.

The thus treated fine silica particles were added in an amount of 0.6% to the above colored fine powder, followed by mixing by a Henschel mixer to provide a developer. Development was carried out with the use of this developer, and then the powder image was transferred to a paper while irradiating a direct current corona of -7 V on the back face of the paper to obtain a copied image. Fixing was effected by means of a commercially available plain paper copying machine (trade name: NP-5000, produced by Canon, Inc.).

The transferred image obtained had a sufficiently high density of 1.5, with no fog at all, and it was a good image with high resolution without any scattering of the toner around the image. The weight of the coating toner layer formed on the sleeve was  $1.5 \times 10^{-3}$  (g/cm<sup>2</sup>).

When successive copying test was performed by preparing continuously transferred images with the use of the above developer, the transferred images after copying 100,000 sheets were fairly comparable to those at the initial stage.

When the environmental conditions were changed to 35°C and 85% R.H., the image density was 1.40 which was substantially to that obtained at normal temperature and normal humidity, clear images were obtained without fog or scattering of the toner, and there was substantially no change in performances until 100,000 sheets of copying during successive copying test. The weight of the toner layer per unit area was  $1.3 \times 10^{-3}$  g/cm<sup>2</sup>. Next, when a transferred image was obtained at lower temperature and lower humidity of 10°C and 10% R.H., the image density was as high as 1.47, with the solid black portion being smoothly developed and transferred, thus giving an excellent image without scattering or drop-off of the toner.

When successive copying tests were performed under these environmental conditions, continuously and intermittently, the density fluctuation was  $\pm 0.1$  until copying of 100,000 sheets and was practically satisfactory, without appearance of white streak or irregularity.

The change in weight of the toner layer per unit area during the tests is shown in Fig. 5(a), which indicates that there was substantially no change.

Comparative Example 1F

A developer was prepared in the same manner as in Example 1F, except that Aerosil 200 was not treated with  $\gamma$ -aminopropyltriethoxysilane or dimethyldichlorosilane, and development and transfer were also

conducted similarly. As the result, only reversed images could be obtained, and the amount of triboelectric charges was  $-3.2 \mu\text{c/g}$ , exhibiting a negative charging characteristic.

5 Comparative Example 2F

A developer was prepared in the same manner as in Example 1F except that no treatment with dimethyldichlorosilane was applied, and images were obtained similarly. At normal temperature and normal humidity,  
10 fog occurred little, but the image density was as low as 0.76 with conspicuous coarsening at the solid black portions. When successive copying test was conducted, the density was lowered to 0.58 on copying of 5000 sheets. When images were obtained under the condi-  
15 tions of  $35^{\circ}\text{C}$  and 85%, the image density was lowered to 0.63 with increase of fog, scattering of the toner and coarsening of the image, proving to be practically unuseful. The transfer efficiency was also as low as 70%. The weight of the toner layer per unit area  
20 was  $0.70 \times 10^{-3} \text{ g/cm}^2$ . When the images were obtained under the conditions of  $10^{\circ}\text{C}$  and 10% R.H., the image density was as low as 0.70, with excessive scattering, fog and coarsening, and transfer drop-off was markedly observed. Continuous image formation was effected  
25 until after about copying of about 5000 sheets, the density became 0.40 to make copying no longer practically possible. The toner weight per unit area

at the initial stage was  $1.7 \times 10^{-3} \text{ g/cm}^2$ , which became increased to  $3.5 \times 10^{-3} \text{ g/cm}^2$ , with formation of wave pattern or irregularity.

Comparative Example 3F

5            Example 1F was repeated except that the amount of dimethyldichlorosilane was changed to 0.1% based on the silica. The hydrophobicity of the treated silica was found to be 15. Until copying 100,000 sheets under normal temperature and normal  
10 humidity conditions in successive copying test, good images could be obtained without change of the toner weight of the toner layer per unit area. However, at 35°C and 85%, the image density at the initial stage was 1.2, which was lowered to 0.78 on copying  
15 of 5,000 sheets. The toner layer weight, which was  $1.4 \times 10^{-3} \text{ g/cm}^2$  at the initial stage, was lowered to  $0.75 \times 10^{-3} \text{ g/cm}^2$ , on copying of 5,000 sheets.

After storage under the conditions of 10°C and 10% for one month, successive copying test was  
20 conducted under the same conditions, whereby the image density at the initial stage was as good as 1.4, but ripple pattern or irregularity occurred on copying of 5,000 sheets, with lowering of the image density to 0.62, and white streaks appeared on the  
25 image on copying of 7,000 sheets. And, the weight of the toner layer was found to be increased to  $3.9 \times 10^{-3} \text{ g/cm}^2$ . The changes in the weight of the

toner layer per unit area during this operation are shown in Fig. 5(b).

Example 2F

The experiment was carried out in substantially the same manner as in Example 1F, except for using N,N-dimethylaminophenyl triethoxysilane in place of  $\gamma$ -aminopropyltriethoxysilane. As the result, the coating was stable to give good results. The hydrophobicity of the silica was found to be 75.

10 Example 3F

The experiment was carried out in substantially the same manner as in Example 1F, except for using aminoethylaminomethylphenethyl triethoxysilane in place of  $\gamma$ -aminopropyl triethoxysilane. As the result, the coating was stable to give good results. The hydrophobicity of the silica was found to be 45.

Example 1G

|    |                                      |           |
|----|--------------------------------------|-----------|
|    | Styrene-butyl methacrylate copolymer | 100 parts |
|    | Magnetite                            | 60 parts  |
| 20 | Carbon black                         | 2 parts   |
|    | Nigrosine                            | 3 parts   |

The above materials were well blended in a blender and then kneaded on a twin roll heated to 150°C. The kneaded product was left to cool, coarsely crushed by a cutter mill, pulverized by means of a micropulverizer with a jet air stream and further subjected to classification by use of a wind force

classifier to obtain colored fine powder of 5 to 20 $\mu$ .

As the next step, fine silica particles Aerosil 200 were subjected to the heat treatment at 800°C for one hour, and the resultant particles were  
5 treated similarly as in Example 1F to obtain treated fine silica particles with a hydrophobicity of 55.

The thus treated silica particles were added to the above colored fine powder in an amount of 0.6%, followed by mixing in a Henschel mixer, to provide  
10 a developer.

Then, an OPC photosensitive member as used in Example 1A was applied with -6 KV corona discharging to be charged over the entire surface thereof, and irradiated with an original image to form  
15 electrostatic latent images thereon.

Development and transfer were conducted in the same manner as in Example 1F, except that this photosensitive member was combined with the developer carrying member of Example 1F and the developer as  
20 prepared above was employed. The image densities of the transferred images and the toner weights on the sleeve under various atmospheric conditions are shown below, and the developing characteristics including the results of successive copying test  
25 were satisfactory, being substantially equal to those of Example 1F

|                | <u>Density</u> | <u>Toner weight</u>                  |
|----------------|----------------|--------------------------------------|
| 22°C, 60% R.H. | 1.38           | $1.5 \times 10^{-3} \text{ g/cm}^2$  |
| 35°C, 85% R.H. | 1.30           | $1.40 \times 10^{-3} \text{ g/cm}^2$ |
| 10°C, 10% R.H. | 1.31           | -                                    |

5           The changes in weight of the toner layer per unit area in successive copying test at lower temperature and lower humidity of 10°C and 10% R.H. are shown in Fig. 6(a), which indicates that there was no substantial change. Also, when developed after storage at 35°C, 90% R.H. the results obtained were substantially the same as before storage.

Comparative Example 1G

10           A developer was prepared in the same manner as in Example 1G, except that Aerosil 200 was not treated with  $\gamma$ -aminopropyltriethoxysilane and dimethyldichlorosilane, and development and transfer were also conducted similarly. As the result, only reversed images could be obtained, and the amount of triboelectric charges was  $-3.2 \text{ } \mu\text{C/g}$ , exhibiting a negative charging characteristic.

Comparative Example 2G

20           A developer was prepared in the same manner as in Example 1G except that no treatment with dimethyldichlorosilane was applied, and images were obtained similarly. At normal temperature and normal humidity, fog occurred little, but the image density was as low as 0.82 with conspicuous coarsening at the

solid black portions. When successive copying test was conducted, the density was lowered to 0.61 on copying of 5000 sheets.

When images were obtained under the conditions of 35°C and 85%, the image density was lowered to 0.63 with increase of fog, scattering of the toner and coarsening of the image, proving to be practically unuseful. The transfer efficiency was also as low as 70%. The weight of the toner layer per unit area was  $0.70 \times 10^{-3} \text{ g/cm}^2$ .

When the images were obtained under the conditions of 10°C and 10% R.H., the image density was as low as 0.68, with excessive scattering, fog and coarsening, and transfer drop-off was markedly observed. Continuous image formation was effected until about 500 sheets was obtained when the density became 0.40 to make copying no longer practically possible. The toner weight per unit area at the initial stage was  $1.7 \times 10^{-3} \text{ g/cm}^2$ , which increased to  $3.5 \times 10^{-3} \text{ g/cm}^2$  on copying of 500 sheets, with formation of wave pattern.

#### Comparative Example 3G

Example 1G was repeated except that the amount of dimethyldichlorosilane was changed to 0.1% based on the silica. The hydrophobicity of the treated silica was found to be 15. Up to 100,000 sheets of copying under normal temperature and normal

humidity in successive copying test, good images could be obtained without change of the toner weight of the toner layer per unit area. However, at 35°C and 85%, the image density at the initial stage was 1.2, which  
5 was lowered to 0.78 on copying of 5,000 sheets. The toner layer, which was  $1.4 \times 10^{-3} \text{ g/cm}^2$ , was lowered to  $0.75 \times 10^{-3} \text{ g/cm}^2$ , on copying of 5,000 sheets.

After storage under the conditions of 10°C and 10% for one month, successive copying test was  
10 conducted under the same conditions, whereby the image density at the initial stage was as good as 1.4, but ripple pattern occurred on copying of 5,000 sheets, with lowering of the image density to 0.62, and  
white streaks appeared on the image on copying of  
15 7,000 sheets. At this stage, the weight of the toner layer was found to be increased to  $4.0 \times 10^{-3} \text{ g/cm}^2$ . The changes in weight of the toner layer per unit area during this operation are shown by Fig. 6(b).

Examples 2G - 9G

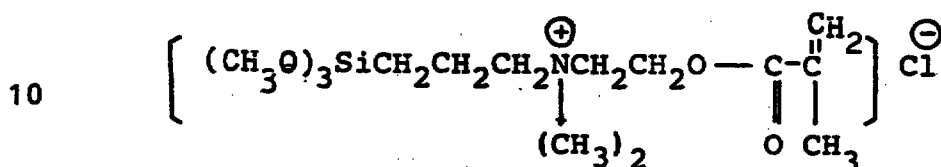
20 When Example 1G was repeated except that the heat treatment temperatures of Aerosil 200 were changed to 430°C, 480°C, 500°C, 600°C, 700°C, 900°C, 1000°C, 1200°C, respectively, good results could be obtained. The hydrophobicity were found to be 50,  
25 50, 55, 58, 70, 65, 68 and 68, respectively. The storage tests of respective samples for one month at 30°C and 90% R.H. also yielded good results.

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Example 1H

|   |                                     |       |
|---|-------------------------------------|-------|
|   | 3-Chloropropyl trimethoxysilane     | 50 g  |
|   | Methyl iodide                       | 0.5 g |
|   | 2-(Dimethylamino)ethyl methacrylate | 50 g  |
| 5 | Dimethylformamide                   | 100 g |
|   | Sulfur                              | 0.5 g |

The above mixture was allowed to react under reflux at 95°C for 50 hours to obtain a product:



Next, 100 g of fine silica particles Aerosil 200 (produced by Nippon Aerosil Co.) were immersed in an aqueous solution containing 4 g of the above product, and the mixture was stirred at 60°C for one hour. Then, the mixture was filtered and dried at 100°C for 10 hours to obtain fine silica particles treated with a cation type unsaturated amine. The silica was placed into a Henschel mixer, and dimethyl-  
 20 dichlorosilane was sprayed onto the silica under stirring to a quantity of 10%. High speed stirring was continued at room temperature for 2 hours, and the mixture was further stirred at 80°C for 24 hours, followed by opening of the mixer to atmospheric  
 25 pressure.

The above treated fine silica particles were added to the colored fine powder of Example 1F

in an amount of 0.6%, followed by mixing in a Henschel mixer, to provide a developer.

Then, an OPC photosensitive member was applied with -6 KV corona discharging to be charged over the entire surface thereof, and irradiated with an original image to form electrostatic latent images thereon.

Development and transfer were conducted in the same manner as in Example 1F, except that this photosensitive member was combined with the developer carrying member of Example 1F and the developer as prepared above was employed. The image densities of the transferred images and the toner weights on the sleeve under various atmospheric conditions are shown below, and the developing characteristics including the results of successive copying test were satisfactory, being substantially equal to those of Example 1F.

|    |                | <u>Density</u> | <u>Toner weight</u>                  |
|----|----------------|----------------|--------------------------------------|
| 20 | 22°C, 60% R.H. | 1.29           | $1.4 \times 10^{-3} \text{ g/cm}^2$  |
|    | 35°C, 85% R.H. | 1.25           | $1.35 \times 10^{-3} \text{ g/cm}^2$ |
|    | 10°C, 10% R.H. | 1.31           | -                                    |

The changes in weight of the toner layer per unit area in successive copying test at lower temperature and lower humidity of 10°C and 10% R.H. are shown in Fig. 7(a), which indicates that there was no substantial change.

Comparative Example 1H

A developer was prepared in the same manner as in Example 1H, except that Aerosil 200 was not treated with the compound prepared in Example 1H or  
5 dimethyldichlorosilane, and development and transfer were also conducted similarly. As the result, only reversed images could be obtained.

Comparative Example 2H

A developer was prepared in the same manner  
10 as in Example 1H except that no treatment with dimethyldichlorosilane was applied, and images were obtained similarly. At normal temperature and normal humidity, fog occurred little, but the image density was as low as 0.70, showing a tendency of coarsening.  
15 When successive copying test was conducted, the density was lowered to 0.53 on copying of 500 sheets. The initial weight of the toner layer per unit area was  $1.3 \times 10^{-3} \text{ g/cm}^2$ , which increased to  $4.8 \times 10^{-3} \text{ g/cm}^2$  on copying of 500 sheets.

20 When the images were obtained under the conditions of 10°C and 10% R.H., the image density was as low as 0.58, with excessive scattering, fog and coarsening, and transfer drop-off was markedly observed. Continuous image formation was effected  
25 until about 500 copies were obtained, when, spot-like irregularity was formed. The toner weight per unit area was  $4.5 \times 10^{-3} \text{ g/cm}^2$ .

Comparative Example 3H

Example 1H was repeated except that the amount of dimethyldichlorosilane was changed to 0.3% based on the silica. The hydrophobicity of the treated silica was found to be 18. Up to 50,000 sheets of copying under normal temperature and normal humidity in successive copying test, good images could be obtained without change of the toner weight of the toner layer per unit area. However, at 35°C and 85%, the image density at the initial stage was 1.0, which was lowered to 0.63 on copying of 5,000 sheets. The toner layer, which was  $1.4 \times 10^{-3} \text{ g/cm}^2$  at the initial stage, was lowered to  $0.63 \times 10^{-3} \text{ g/cm}^2$ , on copying of 5,000 sheets. After storage under the conditions of 10°C and 10% for one month, successive copying test was conducted under the same conditions, whereby the image density at the initial stage was as good as 1.3, but ripple pattern occurred on copying of 5,000 sheets, with lowering of the image density to 0.50, and white streaks appeared on the image on copying of 10,000 sheets. And, the weight of the toner layer was found to be increased to  $4.3 \times 10^{-3} \text{ g/cm}^2$ . The changes in weight of the toner layer per unit area during this operation are shown in Fig. 7(b)

Examples 2H - 4H

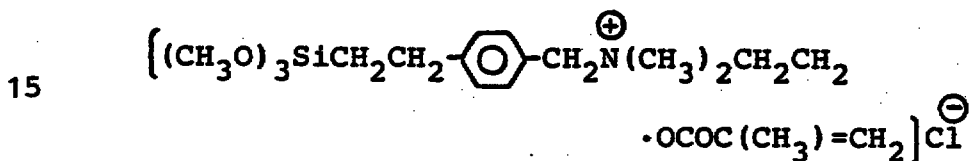
When Example 1H was repeated under

substantially the same conditions except that the amounts of the compound prepared in Example 1H and dimethyldichlorosilane treated on Aerosil 200 were changed to 0.3%, 1.0%; 1.0%, 1.0%; and 5.0%, 1.0%, respectively, good results could be obtained.

Example 5H

|    |                                                                                             |       |
|----|---------------------------------------------------------------------------------------------|-------|
|    | $\text{CH}_2=\text{C}(\text{CH}_3)\text{COOCH}_2\text{CH}_2\text{N}(\text{CH}_3)_2$         | 4 g   |
|    | $(\text{CH}_3\text{O})_3\text{SiCH}_2\text{CH}_2-\text{C}_6\text{H}_4-\text{CH}_2\text{Cl}$ | 5 g   |
|    | Methyl iodide                                                                               | 0.5 g |
| 10 | t-Butyl alcohol                                                                             | 50 g  |
|    | Sulfur                                                                                      | 0.3 g |

The above mixture was refluxed at 100°C for one hour to obtain a product:



Subsequently, fine silica particles of Aerosil 200 were mixed in a Henschel mixer with the above product by spraying an aqueous solution thereof to a quantity of 5%. Then, the mixture was dried at 100°C for 10 hours to obtain fine silica particles treated with a cation type unsaturated amine. The thus treated silica was again charged into a Henschel mixer, and dimethyldichlorosilane was sprayed onto the silica under stirring to a quantity of 5%. Then, the same treatments as in Example 1H were applied. The hydrophobicity was found to be 50.

|                    |           |
|--------------------|-----------|
| Polyethylene oxide | 100 parts |
| Carbon black       | 3 parts   |
| Magnetite          | 70 parts  |
| Nigrosine          | 3 parts   |

5           With the use of the above materials, the same procedure as described in Example 1H was repeated to obtain fine powder of 5 to 25 $\mu$ . A developer was prepared by adding 0.3% of the above treated silica to the fine powder.

10           Next, images were obtained similarly as in Example 1H, followed by pressure fixing. The image density was found to be sufficiently high up to 1.41, and also faithful to the latent image. As the result of successive copying tests, the images  
15   obtained were practically satisfactory until copying of 100,000 sheets, and excellent characteristics were exhibited under the highest temperature and higher humidity conditions of 35°C and 85% R.H., as well as under lower temperature and lower humidity  
20   conditions of 10°C and 10% R.H.

Example 1I

|                                      |           |
|--------------------------------------|-----------|
| Styrene-butyl methacrylate copolymer | 100 parts |
| Magnetite                            | 60 parts  |
| Nigrosine                            | 3 parts   |

25           The above materials were well blended in a blender and then kneaded on a twin roll heated to 150°C. The kneaded product was left to cool,

coarsely crushed by a cutter mill, pulverized by means of a micropulverizer with a jet air stream and further subjected to classification by use of a wind force classifier to obtain colored fine powder of 5 to 20 $\mu$ .

5           As the next step, fine silica particles Aerosil 200 (produced by Nippon Aerosil Co.) were placed in a sealed type Henschel mixer heated to 70°C. and stirred at a high speed, while adding to the silica dropwise  $\gamma$ -aminopropyl triethoxysilane diluted  
10 with alcohol to a treated quantity of 10.0% of the silane coupling agent based on the silica. The fine particles obtained were dried at 120°C and thereafter placed again into a Henschel mixer, and dimethyl  
15 silicone oil (viscosity: 100 centipoise at 25°C) was added to the silica under stirring to a quantity of 10.0%. The mixture was subjected to a high speed stirring at room temperature for 2 hours, followed further by stirring continued at 160°C for 15 hours, and then the mixer was opened to atmospheric pressure.  
20 This mixture was further dried at room temperature under atmospheric pressure for 3 hours.

          The thus treated fine silica particles were added to the above colored powder of 5 to 20 $\mu$ , in an amount of 0.4%, followed by mixing by a Henschel  
25 mixer, to provide a developer.

          Then, an OPC photosensitive member was applied with -6 KV corona discharging to be charged

over the entire surface thereof, and irradiated with an original image to form electrostatic latent images thereon.

Development and transfer were conducted in the same manner as in Example 1F, except that this photosensitive member was combined with the developer carrying member of Example 1F and the developer as prepared above was employed. The image densities of the transferred images and the toner weights on the sleeve under various atmospheric conditions are shown below, and the developing characteristics including the results of successive copying test were satisfactory, being substantially equal to those of Example 1F.

|                | <u>Density</u> | <u>Toner weight</u>                  |
|----------------|----------------|--------------------------------------|
| 22°C, 60% R.H. | 1.35           | $1.38 \times 10^{-3} \text{ g/cm}^2$ |
| 35°C, 85% R.H. | 1.30           | $1.3 \times 10^{-3} \text{ g/cm}^2$  |
| 10°C, 10% R.H. | 1.40           | -                                    |

The changes in weight of the toner layer per unit area in successive copying test at lower temperature and lower humidity of 10°C and 10% R.H. are shown in Fig. 8(a), which indicates that there was no substantial change.

Comparative Example 1I

A developer was prepared in the same manner as in Example 1I, except that Aerosil 200 was not treated with  $\gamma$ -aminopropyltriethoxysilane and dimethyl

silicone oil of 100 centipoise, and development and transfer were also conducted similarly. As the result, only reversed images could be obtained.

Comparative Example 2I

5           A developer was prepared in the same manner as in Example 1I except that no treatment with dimethyl silicone oil was applied, and images were obtained similarly. At normal temperature and normal humidity, fog occurred little, but the image density was as  
10 low as 0.82, the line image was scattered with conspicuous coarsening at the solid black portion. When successive copying test was conducted, the density was lowered to 0.61 on copying of 5000 sheets. When the images were obtained under the conditions of  
15 35°C and 85% R.H., the image density was lowered to 0.63 with increase of fog, scattering and coarsening, thus being unacceptable at all. The transfer efficiency was also as low as 70%. When the images were obtained under the conditions of 10°C and 10% R.H.,  
20 the image density became as low as 0.68 with excessive scattering, fog and coarsening, and transfer drop-off was markedly observed. The initial weight of the toner layer per unit area was  $1.7 \times 10^{-3} \text{ g/cm}^2$ , which increased to  $3.5 \times 10^{-3} \text{ g/cm}^2$  on copying of  
25 500 sheets, with ripple pattern formed.

Comparative Example 3I

Example 1I was repeated except that the

amount of dimethyl silicone oil was changed to 0.5% based on the silica. Until 100,000 sheets of copying under normal temperature and normal humidity in successive copying test, good images could be obtained without change of the toner weight of the toner layer per unit area. However, at 35°C and 85%, the image density at the initial stage was 1.1, which was lowered to 0.80 on copying of 7,000 sheets. The toner layer, which was  $1.4 \times 10^{-3} \text{ g/cm}^2$ , was lowered to  $0.75 \times 10^{-3} \text{ g/cm}^2$ , on copying of 7,000 sheets.

After storage under the conditions of 10°C and 10% for one month, successive copying test was conducted under the same conditions, whereby the image density at the initial stage was as good as 1.4, but ripple pattern occurred on copying of 5,000 sheets, with lowering of the image density to 0.75, and spot irregularities and white streaks appeared on the image on copying of 10,000 sheets. And, the weight of the toner layer was found to be increased to  $4.0 \times 10^{-3} \text{ g/cm}^2$ . The changes of the toner layer per unit area during this operation are shown in Fig. 8(b).

#### Example 2I

When Example 1I was repeated under substantially the same conditions except that the silicone oil was changed to methyl hydrogen silicone oil (trade name: TSF 484, produced by Toshiba Silicone

Co.), good results were obtained.

Example 3I

When Example 1I was repeated under substantially the same conditions except for replacing  $\gamma$ -aminopropyltriethoxysilane with N,N-dimethylamino-phenyl triethoxysilane, good results were obtained.

Example 1J

|    |                                     |           |
|----|-------------------------------------|-----------|
|    | Styrene-butadiene copolymer (70:30) | 100 parts |
|    | Magnetite                           | 60 parts  |
| 10 | Nigrosine                           | 4 parts   |

The above materials were well blended in a blender and then kneaded on a twin roll heated to 150°C. The kneaded produce was left to cool, coarsely crushed by a cutter mill, pulverized by means of a micropulverizer with a jet air stream and further subjected to classification by use of a wind force classifier to obtain colored fine powder of 5 to 20 $\mu$ .

As the next step, fine silica particles Aerosil 200 (produced by Nippon Aerosil Co.) were placed in a sealed type Henschel mixer heated to 70°C and stirred at a high speed, while adding to the silica dropwise isopropyl tri-isostearoyl titanate diluted with alcohol to a treated quantity of 2.0% of the titanium coupling agent based on silica. The fine particles obtained were dried at 120°C.

A developer was prepared by adding the treated fine silica particles to the above fine colored powder in an amount of 0.6%, followed by mixing by a Henschel mixer.

5           Then, an OPC photosensitive member was applied with -6 KV corona discharging to be charged over the entire surface thereof, and irradiated with an original image to form electrostatic latent images thereon.

10           Development and transfer were conducted in the same manner as in Example 1F, except that this photosensitive member was combined with the developer carrying member of Example 1F and the developer as prepared above was employed. The image densities of  
15 the transferred images and the toner weights on the sleeve under various atmospheric conditions are shown below, and the developing characteristics including the results of successive copying test were satisfactory, being substantially equal to those of  
20 Example 1F.

|                | <u>Density</u> | <u>Toner weight</u>                  |
|----------------|----------------|--------------------------------------|
| 22°C, 60% R.H. | 1.40           | $1.5 \times 10^{-3} \text{ g/cm}^2$  |
| 35°C, 85% R.H. | 1.30           | $1.43 \times 10^{-3} \text{ g/cm}^2$ |
| 10°C, 10% R.H. | 1.43           | -                                    |

25   Comparative Example 1J

A developer was prepared in the same manner as in Example 1J, except that Aerosil 200 was not

treated with isopropyl tri-isostearoyl titanate, and development and transfer were also conducted similarly. As the result, only reversed images could be obtained.

Examples 2J - 7J

5                    Example 1J was repeated except that, in place of isopropyl tri-isostearoyl titanate, there were employed as titanate type coupling agents, respectively, isopropyl di-isostearoyltamylphenyl titanate (Example 2J), isopropyl tridodecylbenzene-  
10                    sulfonyl titanate (Example 3J), isopropyltri(di-octylphosphate)titanate (Example 4J), isopropyl-4-aminobenzenesulfonyldi(dodecylbenzenesulfonyl)titanate (Example 5J), isopropyltri(N-ethylamino-ethylamino)-  
                         titanate (Example 6J) and isostearoyl methacryloxy-  
15                    acetate titanate (Example 7J). Good results were obtained in each case.

CLAIMS:

1. A developer comprising a binder resin, a colorant and a positive charge controller, said positive charge controller comprising fumed silica particles treated with a coupling agent having a hydrolyzable group and a non-hydrolyzable organic group bonded to a tetravalent center atom of Si or Ti, said positive charge controller having a hydrophobicity within the range of from 30 to 80 as measured by the methanol titration test.

2. A developer according to Claim 1, wherein the coupling agent has Si as the center atom.

3. A developer according to Claim 2, wherein the coupling agent is represented by the formula:

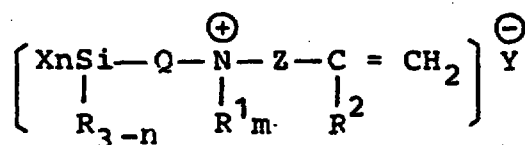


wherein R is an alkoxy group having 1 to 10 carbon atoms or a chlorine atom;  $m$  and  $n$  are integers satisfying the relation of  $m + n = 4$ ; Y is an organic group containing at least one of amino, vinyl, glycidoxy, mercapto, methacryl, and ureido groups.

4. A developer according to Claim 2, wherein the coupling agent is a cation type unsaturated amino-functional silane selected from the compounds represented by the formula:



(28)



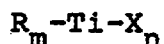
- wherein X is a hydroxyl group or a hydro-  
 5 lyzable group; R is an alkyl having 1 to 6 carbon  
 atoms; n is an integer of 1 to 3; Q is a divalent  
 hydrocarbon group, or an organic group containing  
 oxygen in the form of  $-\text{COC}-$ ,  $-\text{COC}-$ ,  $-\text{C}-$ , or  $-\text{COH}$   
 $\quad \quad \quad \text{O} \quad \quad \quad \text{O} \quad \quad \quad |$   
 10 or nitrogen in the form of  $\text{R}^2\text{N}=$  group;  $\text{R}^1$  is a  
 hydrogen atom, an alkyl group having 1 to 6 carbon  
 atoms or a heterocyclic organic group having a  
 nitrogen atom in the ring; m is 2; Z is a  
 divalent organic group having a conjugated double  
 15 bond with  $-\text{C}=\text{CH}_2$ , and bonded through C-N bonding to  
 $\quad \quad \quad |$   
 $\quad \quad \quad \text{R}^2$   
 the nitrogen atom on its left side;  $\text{R}^2$  is a hydrogen  
 atom or an alkyl having 1 to 6 carbon atoms; and Y  
 is an acid anion,  
 20 or a hydrolyzed product of said cation type un-  
 saturated amino-functional silane.

5. A developer according to any of Claims  
 2 to 4, wherein the positive charge controller has  
 25 a hydrophobicity degree of 30 to 80 by treating the  
 fumed silica particles with the coupling agent and  
 thereafter treating said particles with a hydrophobicity



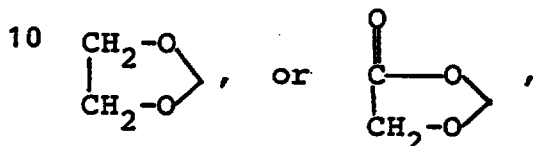
modifying agent selected from organic silicon compounds and silicone oils.

6. A developer according to Claim 1, wherein the coupling agent is a compound represented by the formula:

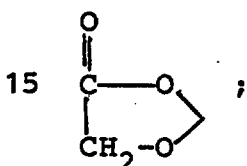


wherein m and n are 1 and 2, 1 and 3, or 4 and 2, respectively;

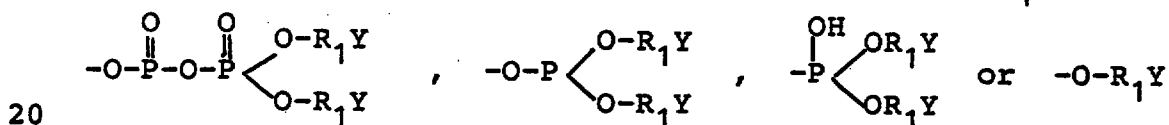
R is an alkoxy group having 1 to 10 carbon atoms,



provided that when m is 1 and n is 2, R is  $\begin{array}{c} CH_2-O \\ | \\ CH_2-O \end{array}$  or



X is  $-O-CH_2-R_1Y$ ,  $-O-CO-R_1Y$ ,  $-O-SO_2-R_1Y$ ,  $-O-P \begin{array}{l} O-R_1Y \\ O-R_1Y \end{array}$



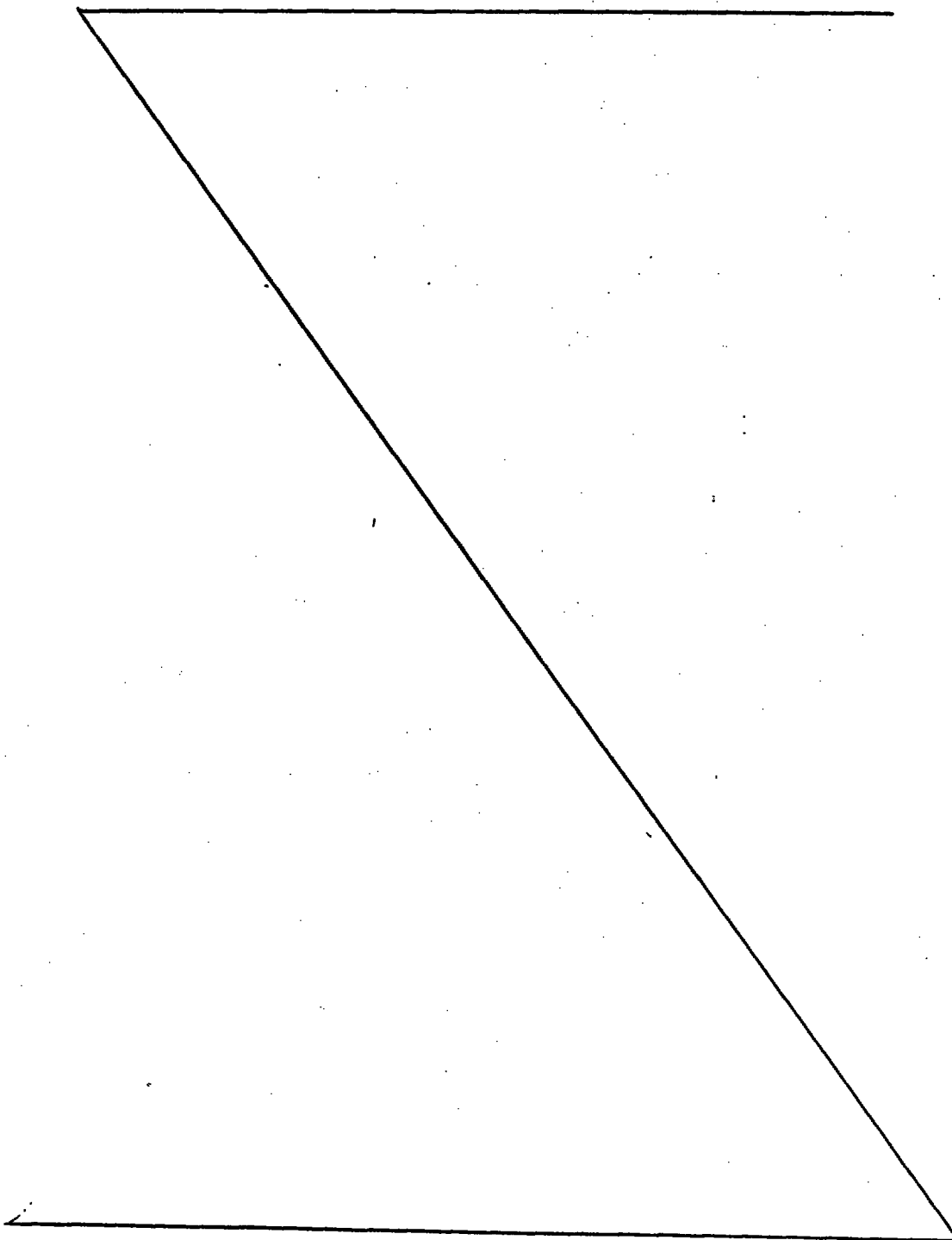
(in the above formulae,  $R_1$  is a saturated or unsaturated divalent aliphatic group having 1 to 31 carbon atoms or a divalent aromatic hydrocarbylene group; Y is a hydrogen atom or an amino group; and a plurality of X,  $R_1$  and Y existing in the same compound being the same or different, respectively).



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7. A developer according to any of Claims 1 to 6, wherein the positive charge controller is obtained by subjecting the fumed silica particles to a heat treatment prior to the treatment with the



coupling agent.

8. A developer according to any of Claims 1  
to 7, wherein the developer further contains magnetic  
5 material powder.

9. A developer according to any of Claims 1  
to 8, wherein the developer comprises binder particles  
having a colorant dispersed therein and the particles  
10 of the positive charge controller adhering on said  
binder particle surfaces.

10. A developing process, which comprises  
providing an electrostatic image bearing member for  
15 bearing electrostatic images on its surface and a  
developer carrying member arranged with a predeter-  
mined gap therebetween, permitting an insulating  
magnetic developer of Claim 8 to be carried on said  
developer carrying member in a thickness thinner  
20 than said gap, and transferring said developer to  
said electrostatic image bearing member thereby to  
effect development.



11. A developer for electrostatography substantially as described herein with reference to any one of the Examples (excluding Comparative Examples).

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