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(54) **Charge controlling agent composition and electrophotographic toner.**

(57) A charge controlling agent composition is disclosed, which comprises a quaternary ammonium salt and one or more inorganic pigments selected from the group consisting of barium sulfate, magnesium hydroxide, aluminum hydroxide, calcium carbonate, magnesium carbonate, barium carbonate, calcium sulfate, zinc silicate, calcium silicate, aluminum silicate, magnesium silicate and magnesium hydrogenphosphate. An electrophotographic toner containing the charge controlling agent composition is also disclosed.

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## FIELD OF THE INVENTION

This invention relates to a charge controlling agent composition useful for toners which are electrophotographic developers. It also relates to an electrophotographic toner containing the composition.

## BACKGROUND OF THE INVENTION

In an image formation process of electrophotography, an electrostatic latent image is formed on an inorganic photoconductive material composed of selenium, a selenium alloy, cadmium sulfide, amorphous  
 10 silicone or the like or an organic photoconductive material using a charge generating agent and a charge transfer agent, developed with a toner, and then the developed image is transferred to paper or a plastic film, followed by fixing to give a visible image.

The photoconductive material has positive electrification property or a negative electrification property according to its construction. When an image part is remained as an electrostatic latent image, the image is  
 15 developed with a toner of the opposite charge. On the other hand, when charge of an image part is removed to conduct reversal development, the image is developed with a toner of the equal charge. Toners are composed of a binder resin, a colorant, and other additives. Generally, a charge controlling agent is further added to the toners in order to impart a desirable friction electrification property (charge velocity, charge level, charge stability), a stability with the passage of time, or an environmental stability. Thus, the  
 20 properties of the toners are greatly influenced by the charge controlling agent.

A two-component type toner is charged by the friction with a carrier, while a one-component type toner is charged by the friction with a sleeve. A latent image on the photoconductive material is developed with the toner thus charged.

Since the toner is consumed, the toner is always fed. However, the toner freshly fed is not charged, and  
 25 hence a rise of charging to a predetermined level is made by stirring in a development zone and friction on sleeve. The amount of charge of the toner is often set to a value in the range of about 10 to 30  $\mu\text{C/g}$ .

The control of the chargeability of the toner is the most important matter for the toner. The charging characteristics of the toner depend on the resin which is the principal component thereof. Usually, desired friction charging characteristics are obtained by using a charge controlling agent. There have been recently  
 30 demanded more higher image quality, higher reliability and more speed-up. Closer charge control has been required in comparison with conventional charge control. Particularly, it has been highly demanded to develop a charge controlling agent which has a rapid rise of charging and is stable against environmental change and passage of time.

One of characteristics required for toners to carry out good development is how the toner freshly fed is  
 35 made to rapidly rise to a predetermined amount of charge. When the toner is made to poorly rise, lowly charged toner is formed and not sufficiently transferred onto a photoreceptor and a lowering in density is caused. In addition, there are caused disadvantages that the toner is scattered, ground staining on duplicates is caused, copying machines are stained and the deterioration of developers is expedited.

In the case of low-speed copying machine, the initial rise of charge quantity can be covered to a certain  
 40 extent by stirring in the development zone. In the case of high-speed copying machine, however, a rapid rise of charging is required because the toner freshly fed is more rapidly transferred from the development zone onto the photoreceptor in proportion as the speed is increased. In the case of the one-component toner, the toner must be charged not by the friction between the toner and the carrier, but only by the friction between the toner and the sleeve. Accordingly, the rise in the one-component toner is more  
 45 important than that in the two-component toner.

There has been conventionally proposed that quaternary ammonium salts are used as charge controlling agents as disclosed in JP-A-62-53944 (the term "JP-A" as used herein means an "unexamined published Japanese patent application"), JP-A-62-71968 and JP-A-62-3259. However, the proposed charge  
 50 controlling agents do not have satisfactory compatibility with resins and are difficultly mixed with the resins in the preparation of the toners. Hence, there are many problems with regard to the characteristics of the toners.

It is very important that the charge controlling agents are uniformly dispersed in the resins in the preparation of the toners. When the charge controlling agents have poor dispersibility, the charge controlling agents can not be uniformly mixed with toner particles, the resulting toner particles are non-homogeneous  
 55 in quality, a rise of charging is low, and the quality of the toner is liable to be changed with the passage of time. Toners obtained by using the proposed quaternary ammonium salts, etc. have problems in that charging is unstable under high temperature and humidity conditions, etc., and the proposed quaternary ammonium salts are not considered to be fully satisfying as charge controlling agents for toners.

Further, it is known that hardly water-soluble inorganic salts are internally added to the toners to prevent the toners from fusing onto the surface of metallic sleeve or the surface of the photoreceptor, to improve durability or to stabilize charging. For example, JP-A-58-91462 discloses a toner wherein barium sulfate is internally added. JP-A-1-200367 discloses a toner wherein tin oxide is internally added.

5 In the former toner, barium sulfate is apt to be agglomerated, and the effect obtained thereby is too low to improve various performances of the toner. The latter toner have problems in that when the toner is used over a long period of time, charging is lowered, which causes scattering of the toner and a defect in image.

Quaternary ammonium salt-modified polymers to be used as a charge controlling agent for a toner have been proposed. For example, JP-A-62-210472 discloses a copolymer of styrene with a methyl chloride-  
10 quaternized product of dimethylaminoethylmethacrylate, JP-A-58-162959 discloses a quaternary salt of a polymer of dialkylaminomethacrylamide, JP-A-59-189354 discloses a quaternary ammonium salt of a vinylpyridine copolymer, and JP-A-59-189351 discloses a quaternary ammonium salt of a dimethylaminomethacrylate copolymer.

However, these products have poor compatibility with the binder resin, thus they have a disadvantage  
15 that their dispersibility in toner are poor.

An attempt has been made to solve these problem by adding to the toner a small amount of fine particles of titanium oxide or abrasives as an external adding agent, as disclosed in JP-A-4-153660 and JP-A-63-318569.

However, since abrasive action of such external adding agents are too strong, they may cause  
20 undesirable wearing out of the photoreceptor upon cleaning of the toner. In addition, these external adding agent may transferred onto paper, which causes stain of the copied image.

Further, a toner comprising a composition obtained by adsorbing an unique fluorine surfactant onto silica gel is disclosed in JP-A-3-1162.

The present inventor have eagerly made studies to solve the above-described problems. As a result,  
25 the present inventors have found that a charge controlling agent composition, which is prepared from a specific quaternary ammonium salt as a charge controlling agent and a specific inorganic pigment and modified, has such a characteristics that the dispersibility of the composition in resins is very good. Further, the present inventors have ascertained that a toner obtained by using the thus-prepared charge controlling agent composition comprising a quaternary ammonium salt modified with an inorganic salt is freed from the  
30 above-described problems, namely, the toner can expedite the rise of charging, can improve the stability of the charging performance of thereof, can be prevented from being scattered and can prevent a defect in image from being caused. The present invention has been accomplished on the basis of this finding.

## SUMMARY OF THE INVENTION

35 Accordingly, an object of the present invention is to provide a charge controlling agent composition of good performance which has a good rise of charging and is not affected by the change of temperatures and humidity even when development is repeatedly carried out continuously and moreover which can reproduce an image stable over a long period of time.

40 Another object of the present invention is to provide a toner in which charge controlling agent composition internally added.

Namely, the present invention relates to a charge controlling agent composition comprising a quaternary ammonium salt and a specific inorganic pigment.

Further, the present invention relates to an electrophotographic toner comprising the charge controlling  
45 agent composition.

## BRIEF DESCRIPTION OF THE DRAWING

Fig. 1 is a graph illustrating a rise of tribo charge quantity of each of the toners obtained in Examples 1  
50 to 3 and Comparative Example 2, wherein the abscissa axis represents a stirring (mixing) time with iron powder carrier, and the ordinate axis represents tribo charge quantity ( $\mu\text{C/g}$ ).

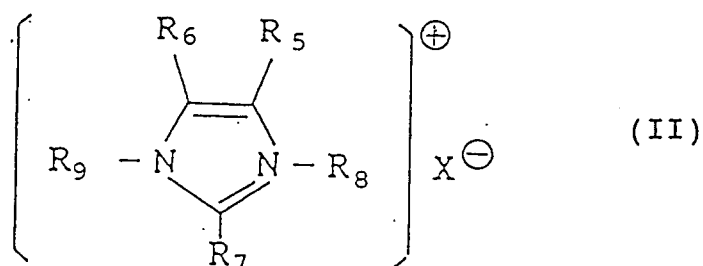
## DETAILED DESCRIPTION OF THE INVENTION

55 Now, the present invention will be illustrated in more detail below.

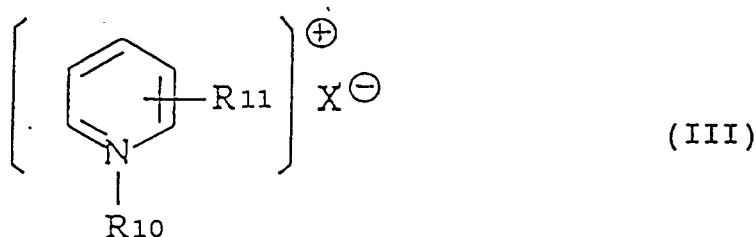
Preferred examples of the quaternary ammonium salt which can be used in the charge controlling agent composition of the present invention include quaternary ammonium salts represented by the following formulas (I) to (VII):



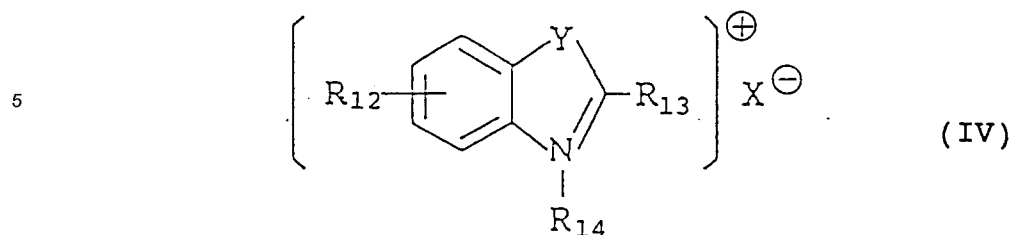
wherein  $R_1$ ,  $R_2$ ,  $R_3$  and  $R_4$  may be the same or different and each represents a hydrogen atom or an alkyl group containing 1 to 30 carbon atoms, an aralkyl group containing 7 to 30 carbon atoms or an aryl group containing 6 to 30 carbon atoms each of which may have one or more members selected from the group consisting of an amino group, an ether bond, a thioether bond, an alkoxy group, a hydroxy group, a carbonic acid amide group, a sulfonamide group, an urethane bond, a chloromethyl group, a nitro group, an aromatic group containing 6 to 30 carbon atoms and an aromatic heterocyclic group containing 6 to 30; and  $X^{\ominus}$  represents an anion;



wherein  $R_5$ ,  $R_6$ ,  $R_7$ ,  $R_8$  and  $R_9$  may be the same or different and each represents a hydrogen atom or an alkyl group containing 1 to 30 carbon atoms, an aralkyl group containing 7 to 30 carbon atoms or an aryl group containing 6 to 30 carbon atoms each of which may have one or more members selected from the group consisting of an amino group, an ether bond, a thioether bond, an alkoxy group, a hydroxy group, a carbonic acid amide group, a sulfonamide group, an urethane bond, a chloromethyl group, a nitro group, an aromatic group containing 6 to 30 carbon atoms and an aromatic heterocyclic group containing 6 to 30 carbon atoms; and  $X^{\ominus}$  represents an anion; provided that  $R_5$  and  $R_6$  or  $R_7$  and  $R_8$  may be combined with each other to form an alicyclic or aromatic ring containing 6 to 30 carbon atoms;



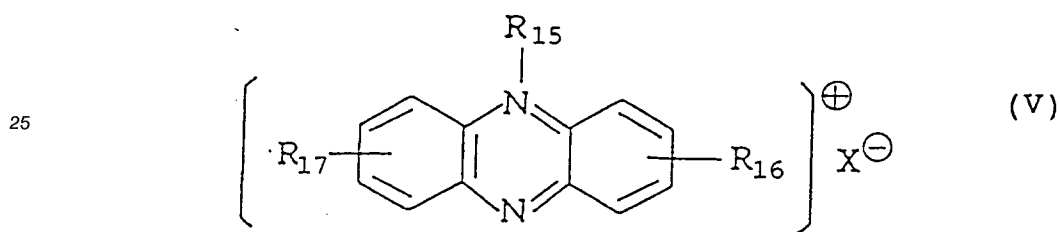
wherein  $R_{10}$  and  $R_{11}$  may be the same or different and each represents an alkyl group containing 1 to 30 carbon atoms, an aralkyl group containing 7 to 30 carbon atoms or an aryl group containing 6 to 30 carbon atoms each of which may have one or more members selected from the group consisting of an amino group, an ether bond, a thioether bond, an alkoxy group, a hydroxy group, a carbonic acid amide group, a sulfonamide group, an urethane bond, a chloromethyl group, a nitro group, an aromatic group containing 6 to 30 carbon atoms and an aromatic heterocyclic group containing 6 to 30 carbon atoms; and  $X^{\ominus}$  represents an anion; provided that  $R_{11}$  may represent a hydrogen atom;



wherein  $\text{R}_{12}$ ,  $\text{R}_{13}$  and  $\text{R}_{14}$  may be the same or different and each represents an alkyl group containing 1 to 30 carbon atoms, an aralkyl group containing 7 to 30 carbon atoms or an aryl group containing 6 to 30 carbon atoms each of which may have one or more members selected from the group consisting of an amino group, an ether bond, a thioether bond, an alkoxy group, a hydroxy group, a carbonic acid amide group, a sulfonamide group, an urethane bond, a chloromethyl group, a nitro group, an aromatic group containing 6 to 30 carbon atoms and an aromatic heterocyclic group containing 6 to 30 carbon atoms; Y presents a carbon, oxygen or sulfur atom; and  $\text{X}^{\ominus}$  represents an anion; provided that  $\text{R}_{13}$  and  $\text{R}_{14}$  may be a hydrogen atom;

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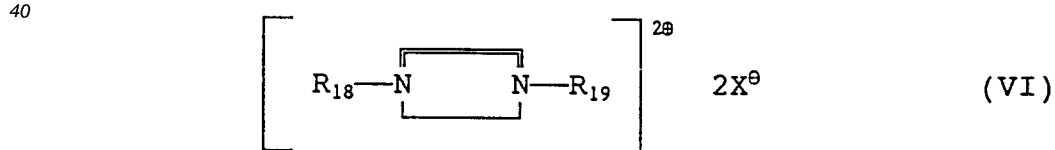
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wherein  $\text{R}_{15}$ ,  $\text{R}_{16}$  and  $\text{R}_{17}$  may be the same or different and each represents an alkyl group containing 1 to 30 carbon atoms, an aralkyl group containing 7 to 30 carbon atoms or an aryl group containing 6 to 30 carbon atoms each of which may have one or more members selected from the group consisting of an amino group, an ether bond, a thioether bond, an alkoxy group, a hydroxy group, a carbonic acid amide group, a sulfonamide group, an urethane bond, a chloromethyl group, a nitro group, an aromatic group containing 6 to 30 carbon atoms and an aromatic heterocyclic group containing 6 to 30 carbon atoms; and  $\text{X}^{\ominus}$  represents an anion; provided that  $\text{R}_{16}$  and  $\text{R}_{17}$  may represent a hydrogen atom;

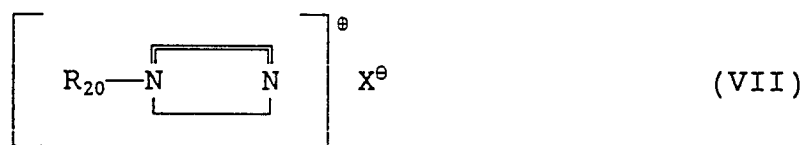
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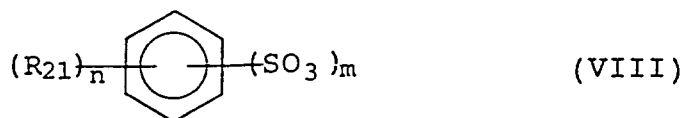
wherein  $\text{R}_{18}$  and  $\text{R}_{19}$  may be the same or different and each represents an alkyl group containing 1 to 30 carbon atoms, an aralkyl group containing 7 to 30 carbon atoms or an aryl group containing 6 to 30 carbon atoms which may have one or more members selected from the group consisting of an amino group, an ether bond, a thioether bond, an alkoxy group, a hydroxy group, a carbonic acid amide group, a sulfonamide group, an urethane bond, a chloromethyl group, a nitro group, an aromatic group containing 6 to 30 carbon atoms and an aromatic heterocyclic group containing 6 to 30 carbon atoms; and  $\text{X}^{\ominus}$  represents an anion; and

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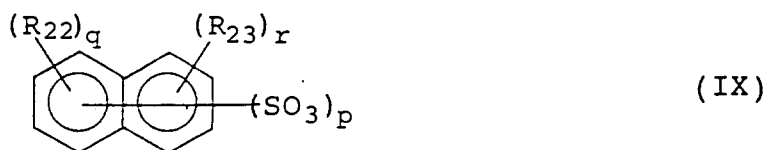


wherein  $\text{R}_{20}$  represents an alkyl group containing 1 to 30 carbon atoms, an aralkyl group containing 7 to 30 carbon atoms or an aryl group containing 6 to 30 carbon atoms which may have one or more members selected from the group consisting of an amino group, an ether bond, a thioether bond, an alkoxy group, a hydroxy group, a carbonic acid amide group, a sulfonamide group, an urethane bond, a chloromethyl group, a nitro group, an aromatic group containing 6 to 30 carbon atoms and an aromatic heterocyclic group containing 6 to 30; and  $\text{X}^{\ominus}$  represents an anion.

In the above formulas (I) to (VII),  $\text{X}^{\ominus}$  represents an anion such as an ion of a halogen atom (e.g.,  $\text{Cl}^{\ominus}$ ,  $\text{Br}^{\ominus}$ ,  $\text{I}^{\ominus}$ ),  $\text{ClO}_4^{\ominus}$ ,  $\text{BF}_4^{\ominus}$ ,  $\text{PF}_6^{\ominus}$ , sulfate ion, nitrate ion, borate ion, phosphate ion, an organic sulfate ion (e.g., methylsulfate ion), an organic phosphate ion (e.g., phenylphosphate ion), a carbonic acid ion (e.g., anions of acetic acid, benzoic acid, stearic acid and oleic acid), a tetraphenyl borate ion (e.g., anions of tetraphenyl borate, p-chlorotetraphenyl borate, p-methyltetraphenyl borate and tetranaphthyl borate), a cyanate ion (e.g., anions of zinc tetracyanate and zinc tetrathiocyanate), a phenolate ion (e.g., anions of phenol, p-chlorophenol and o-chlorophenol), a polyacid ion containing molybdenum or tungsten atom (e.g., anions of molybdenic acid, tungstic acid, and heteropolyacids containing molybdenum or tungsten atom), and an anion of an organic sulfonic acid such as those represented by the following formula (VIII) and (IX):



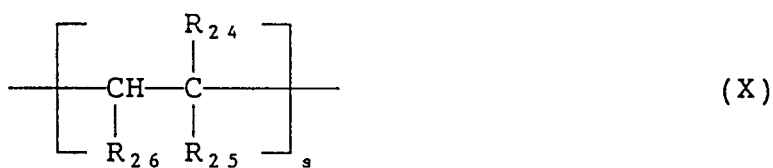
wherein  $m$  presents 1 or 2;  $n$  represents 0, 1 or 2; and  $\text{R}_{21}$  may be the same or different when  $n$  is 2 and represents an alkyl group containing 1 to 30 carbon atoms, an aralkyl group containing 7 to 30 carbon atoms, an aryl group containing 6 to 30 carbon atoms, an alkoxy group containing 1 to 30 carbon atoms, an aryloxy group containing 6 to 30 carbon atoms, hydroxy group or amino group each of which may have one or two of sulfonic acid group; provided that when  $n$  is 2, two  $\text{R}_{21}$  groups may be combined with each other to form a heterocyclic, alicyclic or aromatic heterocyclic ring; and



wherein  $p$  represents 1 or 2;  $q$  and  $r$  each represents 0, 1 or 2;  $\text{R}_{22}$  and  $\text{R}_{23}$  may be the same or different and each represents an alkyl group containing 1 to 30 carbon atoms, an aralkyl group containing 7 to 30 carbon atoms, an aryl group containing 6 to 30 carbon atoms, an alkoxy group containing 1 to 30 carbon atoms, an aryloxy group containing 6 to 30 carbon atoms, hydroxy group or amino group each of which may have one or two of sulfonic acid group; provided that when  $q$  is 1 or 2 and  $r$  is 1 or 2,  $\text{R}_1$  and  $\text{R}_2$  may be combined with each other to form a heterocyclic, alicyclic or aromatic heterocyclic ring.

Further, oligomers having a quaternary ammonium salt group and polymers having a quaternary ammonium salt group can also be used as the quaternary ammonium salt.

Examples thereof include oligomers and polymers represented by the following formula (X):

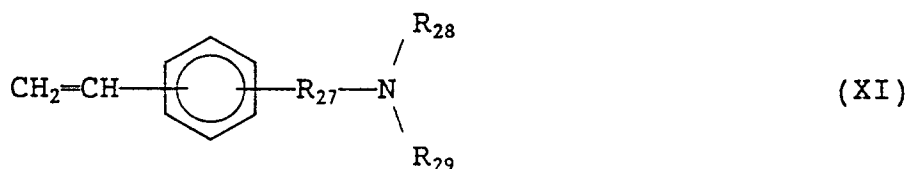


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wherein  $\text{R}_{24}$  and  $\text{R}_{25}$  may be the same or different and each represents an alkyl or alkoxy group containing 1 to 30 carbon atoms, an aralkyl group containing 7 to 30 carbon atoms, an aryl group containing 6 to 30 carbon atoms, or an aryloxy group containing 6 to 30 carbon atoms each of which may have an ether bond, a thioether bond, a carboxylic acid amide group, a sulfonic acid amide group, an urethane bond, a chloromethyl group, a nitro group, or a pyridinium group;  $\text{R}_{26}$  represents a hydrogen atom or an alkyl group containing 1 to 10 carbon atoms; and  $s$  represents an integer of 2 to 100; provided that one of  $\text{R}_{24}$  and  $\text{R}_{25}$  has a quaternary ammonium salt group.

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Further, quaternary ammonium salts of oligomers and polymers obtained from monomers selected from those represented by the following formulas (XI) to (XVI) are preferably used:



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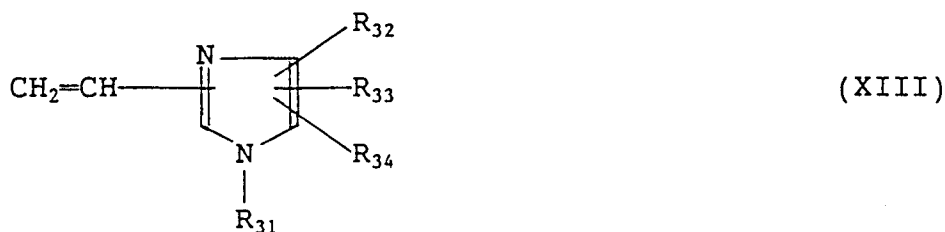
wherein  $\text{R}_{27}$  represents an alkylene group containing 1 to 12 carbon atoms; and  $\text{R}_{28}$  and  $\text{R}_{29}$  independently represent a hydrogen atom or an alkyl group containing 1 to 30 carbon atoms;



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wherein  $\text{R}_{30}$  represents a hydrogen atom or a lower alkyl group;



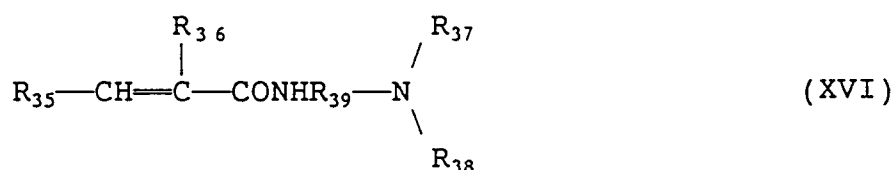
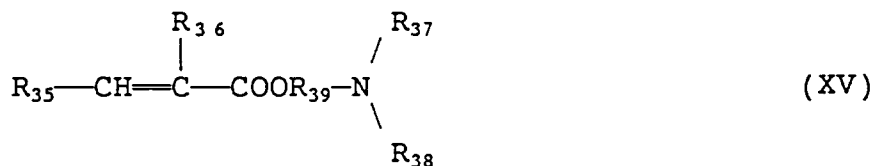
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wherein  $\text{R}_{31}$ ,  $\text{R}_{32}$ ,  $\text{R}_{33}$  and  $\text{R}_{34}$  independently represent a hydrogen atom or an alkyl group containing 1 to 20 carbon atoms;

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wherein  $\text{R}_{35}$  and  $\text{R}_{36}$  independently represent a hydrogen atom or an alkyl group containing 1 to 10 carbon atoms;  $\text{R}_{37}$  and  $\text{R}_{38}$  independently represent a hydrogen atom, an alkyl group containing 1 to 20 carbon atoms or an aryl group; and  $\text{R}_{39}$  represents an alkylene group containing 1 to 20 carbon atoms.

Examples of the inorganic pigment which can be used in the present invention include barium sulfate, magnesium hydroxide, aluminum hydroxide, calcium carbonate, magnesium carbonate, barium carbonate, calcium sulfate, zinc silicate, calcium silicate, aluminum silicate, magnesium silicate and magnesium hydrogenphosphate. These inorganic pigments may be coated with organic compounds, organic polymers, hydrophobic treating agents or titanate coupling agents.

The particle size of the inorganic pigment is preferably  $25 \mu\text{m}$  or below. When the inorganic pigment is present in the form of secondary aggregations, the particle size of the aggregation may be  $25 \mu\text{m}$  or more.

The inorganic pigments may be any of synthetic products and natural pigments. Further, inorganic pigment-containing reaction mixtures (solutions) formed by reaction of inorganic compounds can be used.

For example, a mixture of barium sulfate and aluminum hydroxide obtained by reaction barium chloride with aluminum sulfate and an alkali, a mixture of zinc carbonate and sodium sulfate obtained by reacting sodium carbonate with zinc sulfate, calcium carbonate obtained by reacting sodium carbonate with calcium chloride, or calcium sulfate obtained by reacting sodium sulfate with calcium chloride can be used.

The charge controlling agent composition of the present invention is prepared from the aforesaid quaternary ammonium salt and the aforesaid inorganic pigment. Any methods can be employed to prepare the charge controlling agent composition from the quaternary ammonium salt and the inorganic pigment can be used so long as a homogeneous composition of them can be obtained.

The homogeneous composition may be either a composition comprising particles in which the quaternary ammonium salt and the inorganic pigment are contained, or a composition comprising particles of the quaternary ammonium salt on which the inorganic pigment uniformly adheres.

The particles in which the quaternary ammonium salt and the inorganic pigment are contained is preferably prepared by adding the inorganic pigment or inorganic compounds which form the inorganic pigment at any one stage during the preparation of the quaternary ammonium salt, separating the resulting quaternary ammonium salt containing the inorganic pigment, then drying the quaternary ammonium salt.

In this instance, it is preferred that the inorganic pigment is, or the inorganic compounds which form the inorganic pigment are, allowed to exist together with starting compounds in a reaction system for preparing the quaternary ammonium salt.

As the inorganic compounds which form the inorganic pigment, those mentioned above can be used.

Further, the inorganic pigment may be added to a reaction mixture which is transferred from reaction step for the formation of the quaternary ammonium salt to purification step therefor, or it may be added to a wet filter cake obtained in the purification step.



Furthermore, the particles in which the quaternary ammonium salt and the inorganic pigment are contained can be prepared by mixing the dried quaternary ammonium salt and the inorganic pigment in the presence of an appropriate solvent, and then drying the resulting mixture. In this instance, the mixing of the quaternary ammonium salt and the inorganic pigment can be effected by kneading them in the presence of a slight amount of the solvent, or by preparing a slurry comprising the quaternary ammonium salt, the inorganic pigment and the solvent and stirring the slurry. The solvent may be water, an organic solvent, or a mixture of water and an organic solvent. Preferred examples of the organic solvent include alcohols such as methanol, ethanol, propanol and butanol; ketones such as acetone and MIBK (methyl isobutyl ketone); dimethylformaldehyde and dimethylsulfonamide.

Alternatively, the particles of the quaternary ammonium salt on which the inorganic pigment uniformly adheres can be prepared by mechanically mixing and stirring the dried quaternary ammonium salt and the inorganic pigment so as to adhere the inorganic pigment uniformly onto the surface of the particles of the quaternary ammonium salt. As means for mixing, a ball mill, a Henschel mixer, a speed kneader, and the like can be used.

The particles obtained in the afore-mentioned manners can be used as the charge controlling agent composition for the preparation of the toner as such. If desired, the particles may be further pulverized, classified, and then used.

The content of the inorganic pigment in the thus-obtained charge controlling agent composition is such an amount that the characteristics of the charge controlling agent composition as a charge controlling agent is not adversely affected. The weight ratio of the quaternary ammonium salt to the inorganic pigment in the charge controlling agent composition is preferably from 0.5 to 99.5, more preferably from 5 to 95.

The charge controlling agent composition of the present invention has good dispersibility in binder resins, and a toner obtained by using the charge controlling agent composition has a good rise of charging and is freed from the problems associated with conventional toner with regard to the unstable chargeability of the toner and the scattering of the toner even when the toner is used over a long period of time under a low temperature and humidity condition or a high temperature and humidity condition. Accordingly, a clear developed image can be obtained.

The toner of the present invention is prepared by mixing the aforesaid charge controlling agent composition according to the present invention with the other components.

In a general method for preparing a two-component type toner, a binder resin is placed into a Henschel mixer and then a colorant and a charge controlling agent are added thereto, followed by preliminary mixing. Subsequently, the resulting mixture is kneaded by means of an EXTRUDER generally at 150 °C or below, and then the resulting product is pulverized and classified to give a toner having a particle size distribution ranging from 5 to 25  $\mu\text{m}$ . On the other hand, a one-component type toner can be obtained in the aforementioned method except for that the colorant is replaced by a magnetic powder.

The toner of the present invention can be obtained in the aforementioned methods provided that the charge controlling agent composition of the present invention is used in place of the conventional charge controlling agent.

An amount of the charge controlling agent composition of the present invention in the toner is preferably from 0.1 to 15 % by weight, more preferably from 0.5 to 10 % by weight, based on the weight of the toner.

It is preferred that the charge controlling agent composition of the present invention is in the form particles having a particle size distribution ranging from 0.5 to 25  $\mu\text{m}$ . It is also preferred that the quaternary ammonium salt is in the form of particles having a particle size distribution ranging from 0.5 to 25  $\mu\text{m}$ .

The toner of the present invention comprises a binder resin and a colorant in addition to the charge controlling agent composition.

Examples of the binder resin which can preferably be used in the toner of the present invention include polymers of styrene and substituted styrenes such as polystyrene and polyvinyltoluene; styrene-substituted styrene copolymers; styrene-acrylic ester copolymers; styrene-methacrylic acid copolymers; styrene-acrylonitrile copolymers; polyvinyl chloride resins; polyethylene-silicone resins; polyesters; polyurethanes; polyamides; epoxy resins; modified rosins; phenolic resins; and waxes. In addition thereto, other materials which are conventionally used as binder resins for toners can also be used in the present invention.

Examples of the colorant which can be used in the present invention include C.I. Pigment Yellow-12, C.I. Solvent Yellow-18, C.I. Disperse Yellow-33, C.I. Pigment Red-122, C.I. Solvent Red-19, C.I. Pigment Blue-15, C.I. Pigment Black-1, C.I. Solvent Black-3, C.I. Solvent Black-22 and carbon black. In addition thereto, other materials which are conventionally used as colorants for toners can also be used in the present invention. The colorant is contained in the toner according to the present invention in an amount of preferably from 3 to 10 % by weight.

The mixing of the charge control agent composition and the other ingredient to give the toner of the present invention can be effected by melt-mixing the binder resin with 0.1 to 50 % by weight based on the binder resin of the charge controlling agent composition, solidifying the resulting mixture, coarsely crushing the solidified mixture by means of a crushing device such as a hammer mill, finely crushing the crushed particles by means of a jet mill crusher, and then classifying the finely crushed particles by means of an air stream classifier. Alternatively, it may be effected by adding a polymerization initiator to a monomer or a monomer mixture for the binder resin, adding the charge controlling agent composition to the mixture in an amount of 0.1 to 50 % by weight based on the weight of the monomer component, polymerizing the monomer component while suspending in water, and then recovering and drying the resulting toner. A dye or carbon black as the colorant may added during these steps.

The thus-prepared toner can be charged by an amount of charge suitable for carrying out the development of an electrostatic latent image by the friction between the toner and the carrier. Even when development is repeatedly carried out, the toner is not affected by the change of temperature and humidity, the charge quantity can be retained constantly, and the charge distribution is uniform and can be kept constant.

Examples of the carrier which can be used in the present invention include iron powder and carriers obtained by coating a magnetic core with a styrene-methyl methacrylate copolymer, a silicone resin, a mixed resin of a styrene-methyl methacrylate copolymer and a silicone resin or a tetrafluorostyrene resin.

The charge controlling agent composition of the present invention can provide excellent charging characteristics even when used in one-component developer containing a magnetic substance. Further, the charge controlling agent composition of the present invention can be used for capsule toners and polymerization toners.

Examples of magnetic materials which can be used as the magnetic substance include fine powders of metals such as iron, nickel and cobalt; alloys of metals such as iron, cobalt, copper, aluminum, nickel and zinc; metal oxides such as aluminum oxide, iron oxide and titanium oxide; ferrites of iron, manganese, nickel, cobalt and zinc; nitrides such as vanadium nitride and chromium nitride; carbides such as tungsten carbide and silicon carbide; and mixtures thereof.

Preferred examples of the magnetic substance include iron oxides such as magnetite, hematite and ferrite.

The present invention is further illustrated below by reference to the following preparation examples of the composition and the application examples thereof as the toner. However, the invention is not intended to be construed as being limited to these examples. In the following examples, the amounts, parts and ratios of the ingredients are by weight unless otherwise indicated.

#### EXAMPLE 1

Quaternary ammonium salt:



There was dissolved 13.0 parts of N,N-dimethyl-N,N-ditetradecylammonium chloride in 100 parts of methanol. To the resulting solution, there was added 20 parts of aluminum hydroxide (2  $\mu\text{m}$ ). Subsequently, an aqueous solution composed of 10 parts of ammonium molybdate tetrahydrate and 60 parts of water was added thereto, and the mixture was stirred at 50 °C. The precipitated white precipitate was recovered by filtration, thoroughly washed with water and dried to obtain Composition 1 composed of the quaternary ammonium salt and aluminum hydroxide (50:50).

Subsequently, 88 parts of a styrene-n-butyl methacrylate copolymer resin (Himer SBM-73 manufactured by Sanyo Kasei KK), 5 parts of low-molecular polypropylene (Viscol 550-P manufactured by Sanyo Kasei KK), 5 parts of carbon black (#44 manufactured by Mitsubishi Kasei Corporation) and 2 parts of Composition 1 were premixed in a mixer for 10 minutes, and then melt-kneaded by means of a hot roll mill at 120 °C, followed by crushing and classifying to obtain a toner having a particle size of 5 to 25  $\mu\text{m}$ .

Next, 3 parts of the toner was mixed with 97 parts of an iron powder carrier (TEFV 200/300 manufactured by Nippon Teppun KK) to prepare a developer. After the developer was stirred, tribo-charge quantity was measured by using a blow-off charge measuring machine (manufactured by Toshiba Chemical KK). Tribo charge quantities ( $\mu\text{C/g}$ ) after stirring time for 30 seconds, one minute, 3 minutes, 5 minutes, 10 minutes, 30 minutes and 2 hours were 3.9, 5.5, 9.3, 10.0, 10.4, 10.3 and 10.3, respectively. Accordingly, a rise of charging in a short period to time was good, charge quantity reached nearly saturated charge quantity in 5 minutes, and the rise of charging was very good.

The toner was put into a development device, and continuous copying was carried out to make an image test. A good image was obtained at the initial stage of running. After obtaining 50,000 copies, the image quality was not change, and neither toner scattering nor off-set occurred. Further, the continuous copying test was carried out under high temperature and humidity conditions at 35 °C and 85% RH and under low temperature and humidity conditions at 10 °C and 30% RH. An image quality substantially equal to that obtained in the copying test under normal temperature and humidity conditions was obtained. Neither toner scattering nor off-set occurred.

## EXAMPLE 2

There was dissolved 13.0 parts of N,N-dimethyl-N,N-ditetradecylammonium chloride in 100 parts of methanol. An aqueous solution composed of 100 parts of ammonium molybdate tetrahydrate and 60 parts of water was added thereto, and the mixture was stirred at 50 °C. The produced quaternary ammonium salt (Compound 1) was recovered by filtration.

The resulting wet cake was dispersed in 100 parts of water with stirring at room temperature. Subsequently, 20 parts of the same aluminum hydroxide (2 μm) as that used in Example 1 was added thereto, and the mixture was stirred overnight. The product was recovered by filtration, thoroughly washed with water and dried to obtain Composition 2 composed of the quaternary ammonium salt (Compound 1) and aluminum hydroxide (50:50).

A toner was prepared in the same manner as in Example 1 except that Composition 2 was used in place of Composition 1. The tribo charge quantity of the toner was measured. As a result, it was found that, after stirring of the toner with an iron powder carrier for 30 seconds, one minute, 3 minutes, 5 minutes, 10 minutes, 30 minutes and 2 hours, tribo charge quantities (μC/g) were 3.6, 4.9, 9.0, 9.6, 9.8, 9.9 and 10.2, respectively. Tribo charge quantity after stirring for 5 minutes was 94% of that after 2 hour-stirring. Thus, there was obtained a toner having good rise of charging in a short period of time.

The toner was put into a development device, and continuous copying was carried out to make an image test. A good image was obtained at the initial stage of running. After obtaining 50,000 copies, the quality of the image was not changed, and neither toner scattering nor offset occurred. The toner was not affected under high temperature and humidity environmental conditions as well as under low temperature and humidity environmental conditions, and a good image quality was obtained.

## EXAMPLE 3

The quaternary ammonium salt (Compound 1) was synthesized in the same manner as in Example 2, recovered by filtration and dried. Immediately after drying, the same aluminum hydroxide (2 μm) as that used in Example 1 was added thereto, and the mixture was pulverized to obtain Composition 3 composed of the quaternary ammonium salt and aluminum hydroxide (50:50).

A toner was prepared in the same manner as in Example 1 except that Composition 3 was used in place of Composition 1. Tribo charge quantity was measured. After stirring of the toner with an iron powder carrier for 30 seconds, one minute, 3 minutes, 5 minutes, 10 minutes, 30 minutes and 2 hours, tribo charge quantities (μC/g) were 3.4, 4.8, 8.8, 9.3, 9.5, 9.6 and 10.3, respectively. The value measured after stirring for 5 minutes was 90.3% of that after 2 hours. There was obtained a toner having good rise of charging in a short period of time.

The toner was put into a development device, and continuous copying was carried out to make an image test. A good image was obtained at the initial stage of running. After obtaining 50,000 copies, the image quality was not changed, and neither toner scattering nor offset occurred.

The continuous copying test was carried out under high temperature and humidity conditions at 35 °C and 85% RH and under low temperature and humidity conditions at 10 °C and 30% RH. An image quality substantially equal to that obtained under normal temperature and humidity conditions was obtained. Neither toner scattering nor offset occurred.

## COMPARATIVE EXAMPLE 1

One part of the quaternary ammonium salt (Compound 1) synthesized and dried in the same manner as in Example 2 was used, and a toner was prepared in the same manner as in Example 1 except that aluminum hydroxide was omitted. Tribo charge quantity was measured. After stirring of the developer for 30 seconds, one minute, 3 minutes, 5 minutes, 10 minutes, 30 minutes and 2 hours, tribo charge quantities

( $\mu\text{C/g}$ ) were 2.0, 2.8, 4.9, 6.5, 8.7, 9.2 and 10.0, respectively. Tribo charge quantity after stirring for 5 minutes was 65% of that after 2 hours. Hence, a rise of charging was very poor.

In the same manner as in Example 1, an image test was made. A clear image which was not fogged was obtained at the initial stage of running. However, after obtaining about 1,000 copies, an image which was fogged and not clear was obtained.

## COMPARATIVE EXAMPLE 2

The quaternary ammonium salt (Compound 1) synthesized and dried in the same manner as in Example 2 was used, and a toner was prepared in the same manner as in Example 1 by using the following composition.

Styrene-n-butyl methacrylate copolymer resin (Himer SBM-73F manufactured by Sanyo Kasei KK)	88 parts
Low-molecular polypropylene (VISCOL 550-P manufactured by Sanyo Kasei KK)	5 parts
Carbon black (#44 manufactured by Mitsubishi Kasei Corporation)	5 parts
Quaternary ammonium salt (Compound 1)	1 part
Aluminum hydroxide (2 $\mu\text{m}$ )	1 part

In the same manner as in Example 1, a developer was prepared by using the resulting toner. After stirring with an iron powder carrier for 30 seconds, one minute, 3 minutes, 5 minutes, 10 minutes, 30 minutes and 2 hours, tribo charge quantities ( $\mu\text{C/g}$ ) were 2.0, 3.0, 5.3, 7.0, 9.0, 9.5 and 10.4, respectively. Tribo charge quantity after stirring for 5 minutes was 67% of that after 2 hours. Hence, a rise of charging was poor.

In the same manner as in Example 1, an image test was carried out. A clear image which was not fogged was obtained at the initial stage of running. However, after obtained about 1,000 copies, an image which was fogged and not clear was obtained.

Fig. 1 is a graph illustrating a rise of tribo charge quantity of each of the toners obtained in Examples 1 to 3 and Comparative Example 2, wherein the abscissa axis represents a stirring time (mixing time) of the toner with iron powder carrier, and the ordinate axis represents tribo charge quantity ( $\mu\text{C/g}$ ). It can be seen from these results that the toners containing the charge controlling agent composition of the present invention are very excellent in a rise of charging.

It is important that the toner and the carrier are uniformly dispersed in each other in a short period of time to obtain a rapid rise characteristics of charging. A dispersed state after the stirring of each of the toners of Examples 1 to 3 and Comparative Examples 1 and 2 for 30 seconds was visually observed. Further, a developer was prepared by blending 3 parts of the toner with 97 parts of the carrier (iron powder carrier TEFV 200/300 manufactured by Nippon Teppun KK), and an image was copied by using a copying machine.

The toners containing the charge controlling agent composition of the present invention prepared in Examples 1 to 3 showed that the dispersed state of the toner and the carrier was nearly uniform, while the dispersed state of the toners of Comparative Examples 1 and 2 were speckled and non-uniform. When the toners of Examples 1 to 3 were dispersed, the dispersion of the toner and the carrier in each other could be attained in a short period of time, resulting in an excellent rise of charging as shown in Fig. 1. Further, the toners of Examples 1 to 3 gave a good image which had a good image quality and scarcely suffered from ground fog. The results are thought to be due to the charging characteristics obtained by a difference in the dispersed state of the quaternary ammonium salt and the inorganic pigment.

## EXAMPLE 4

Composition 4 was prepared in the same manner as in Example 1 except that aluminum hydroxide (30  $\mu\text{m}$ ) was used in place of aluminum hydroxide (2  $\mu\text{m}$ ). A toner was prepared in the same manner as in Example 1 except that Composition 4 was used in place of Composition 1. The tribo charge quantity of the toner was measured. After the mixing of the toner with the carrier for 30 seconds, one minute, 3 minutes, 5 minutes, 10 minutes, 30 minutes and 2 hours, tribo charge quantities ( $\mu\text{C/g}$ ) were 3.8, 5.6, 9.2, 9.9, 10.1, 10.2 and 10.2, respectively. The value after stirring for 5 minutes was 97.0% of that after 2 hours, and

hence a rise of charging was good.

The toner was put into a development device, and continuous copying was carried out to make an image test. A good image was obtained at the initial stage of running. After obtaining 50,000 copies, the image quality was not changed, and neither toner scattering nor offset occurred.

Further, the continuous copying test was carried out under high temperature and humidity conditions at 35 °C and 85% RH and under low temperature and humidity conditions at 10 °C and 30% RH. An image quality substantially equal to that obtained by conducting copying under normal temperature and humidity conditions was obtained. Further, neither toner scattering nor offset occurred.

#### EXAMPLES 5 TO 19 AND COMPARATIVE EXAMPLES 3 TO 17

Compositions 5 to 30 containing quaternary ammonium salts indicated in Table 1 were prepared in the same manner as in Example 1 and used in Examples 5 to 19 shown in Table 2.

In the same manner as in Comparative Example 2, toners were prepared in Comparative Examples 3 to 17 shown in Table 3.

The results are shown in Tables 2 and 3. Binder resins, charge quantity-measuring method and the criterion of each evaluation item in Tables 2 and 3 are as follows.

Binder resins used in the preparation of toners:

- |                  |   |
|------------------|---|
| A:               | Styrene-acrylic acid copolymer (Himer SBM-73 manufactured by Sanyo Kasei KK)                                    |
| B:               | Styrene-acrylic acid copolymer (Himer TB-1000 manufactured by Sanyo Kasei KK)                                   |
| C:               | Polyester (HP-313 manufactured by Nippon Gosei Kagaku KK)   |
| D:               | Polyester (HP-320 manufactured by Nippon Gosei Kagaku KK)   |
| E:               | Polystyrene (average molecular weight: 1500)  |
| Charge quantity: | Value measured after stirring for 2 hours.  |
| Criterion:       | The mark ○ means that there is practically no problem.<br>The mark X means that there is practically a problem. |

TABLE 1




Composition No.	Quaternary ammonium salt (A)	Compound (No.)	Inorganic pigment (B)	Composition ratio (by weight) (A):(B)
5	$(C_{18}H_{37})_2(CH_3)_2N^+ \cdot 1/10 [H_2W_{12}O_{42}]^{10-}$	(2)	barium sulfate	25:75
6	$(C_{18}H_{33})_2(CH_3)_2N^+ \cdot 1/6 [P_2Mo_{24}O_{80}]^{6-}$	(3)	mixture (1:1) of $Al(OH)_3$ and $BaSO_4$	40:60
7	$(C_{18}H_{37})(C_{14}H_{29})(CH_3)_2N^+ \cdot 1/4 [Mo_8O_{26}]^{4-}$	(4)	calcium carbonate	100:10
8	$(C_{14}H_{29})_2(CH_3)_2N^+CH_2-$  $\cdot 1/4 [SiW_{12}O_{40}]^{4-}$	(5)	calcium sulfate	30:70
9	$CH_3OC_8H_{16}(CH_3)_3N^+ \cdot 1/5 [BMo_{12}O_{40}]^{5-}$	(6)	calcium sulfate	50:50
10	$(C_{18}H_{33})_2(CH_3)(C_2H_4OH)N^+ \cdot 1/4 [Mo_8O_{26}]^{4-}$	(7)	$CaCO_3$ treated with titanium coupling agent	10:100
11	$(C_{18}H_{37})(CH_3)_2N^+CH_2-$  $\cdot 1/3 [PW_{12}O_{40}]^{3-}$	(8)	magnesium hydroxide	50:50
12	$(\text{benzene ring})_4N^+ \cdot 1/5 [FeW_{12}O_{40}]^{5-}$	(9)	calcium sulfate	30:70
13	$CH_3-$  $N^+-C_{16}H_{33} \cdot 1/4 [D_{10}O_{28}]^{4-}$	(10)	calcium carbonate	10:90

TABLE 1 (cont'd)

Composition No.	Quaternary ammonium salt (A)	Compound (No.)	Inorganic pigment (B)	Composition ratio (by weight) (A):(B)
14	$\text{C}_{17}\text{H}_{35} \text{ (CH}_3)_2 \text{ N} \text{ CH}_2 \text{ - } \langle \bigcirc \rangle \text{ - } \cdot 1/5 [\text{PMo}_{12}\text{O}_{42}]^{\ominus 5}$	(11)	mixture (1:1) of $\text{CaCO}_3$ and $\text{Al (OH)}_3$	50:50
15	$\text{C}_{11}\text{H}_{22}\text{CONH(CH}_2)_3 \text{ (CH}_3)_2 \text{ N} \text{ CH}_2 \text{ - } \langle \bigcirc \rangle \text{ - } \cdot 1/10 [\text{H}_2\text{P}_{12}\text{O}_{42}]^{\ominus 10}$	(12)	magnesium carbonate	40:60
16	$\text{C}_6\text{H}_4 \text{ - } \text{N(CH}_2)_3 \text{ (CH}_3)_3 \text{ N} \cdot 1/3 [\text{PMo}_{12}\text{O}_{40}]^{\ominus 3}$	(13)	mixture (1:1) of $\text{CaCO}_3$ and $\text{Al (OH)}_3$	40:60

TABLE 1 (cont'd)

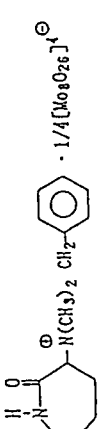
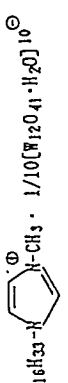
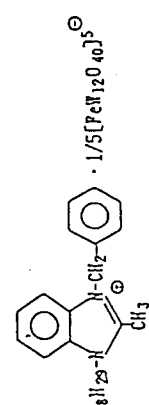
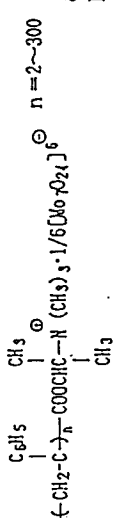
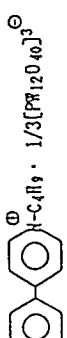
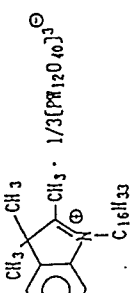
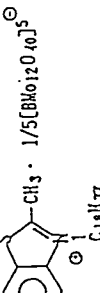
Composition No.	Quaternary ammonium salt (A)	Compound (No.)	Inorganic pigment (B)	Composition ratio (by weight) (A):(B)
17		(14)	mixture (1:1) of CaCO <sub>3</sub> and Al(OH) <sub>3</sub>	25:75
18		(15)	mixture (1:1) of Al(OH) <sub>3</sub> and CaSO <sub>4</sub>	40:60
19		(16)	aluminum hydroxide	80:20
20		(17)	calcium carbonate	50:50
21		(18)	calcium silicate	100:10
22		(19)	mixture (1:1) of CaCO <sub>3</sub> and Al(OH) <sub>3</sub>	80:20
23		(20)	zinc silicate	20:80



TABLE 1 (cont'd)

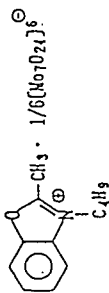
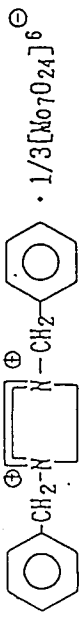
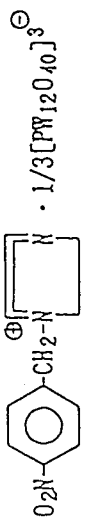
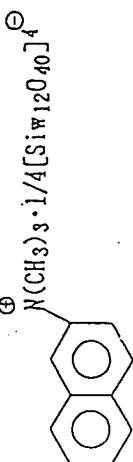
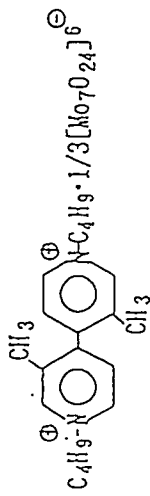
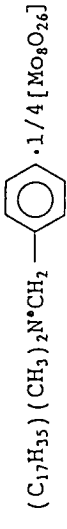
Composition No.	Quaternary ammonium salt (A)	Compound (No.)	Inorganic pigment (B)	Composition ratio (by weight) (A):(B)
24		(21)	aluminum silicate	50:50
25		(22)	calcium carbonate	30:70
26		(23)	barium carbonate	50:50
27		(24)	mixture (1:1) of CaCO <sub>3</sub> and Al(OH) <sub>3</sub>	10:90
28	ditto	(24)	calcium carbonate	70:30
29		(25)	mixture (1:1) of CaCO <sub>3</sub> and Al(OH) <sub>3</sub>	50:50
30		(26)	magnesium hydrogen- phosphate	100:10

TABLE 2

Example	Composition No.	Resin	Colorant	Charge quantity ( $\mu\text{C/g}$ )	Rise of charging	Evaluation of toner		
						Image quality	After Preservation of the environment	Fog/toner scattering
5	8	A	carbon black (#44, Mitsubishi Kasei Corp.)	10.8	0	0	0	0/0
6	10	A	ditto	13.5	0	0	0	0/0
7	13	A	ditto	9.0	0	0	0	0/0
8	14	A	carbon black (R-300, Cabot Corp.)	10.0	0	0	0	0/0
9	15	C	ditto	13.2	0	0	0	0/0
10	17	C	ditto	14.0	0	0	0	0/0
11	21	C	carbon black (ELFTEI-8, Cabot Corp.)	10.5	0	0	0	0/0
12	21	E	ditto	10.3	0	0	0	0/0
13	22	A	carbon black (#44, Mitsubishi Kasei Corp.)	11.0	0	0	0	0/0
14	24	A	ditto	9.8	0	0	0	0/0
15	26	A	carbon black (#44, Mitsubishi Kasei Corp.)	13.0	0	0	0	0/0

TABLE 2 (cont'd)

Example	Composition No.	Resin	Colorant	Evaluation of toner			
				Charge quantity ( $\mu\text{C/g}$ )	Rise of charging	Image quality Initial stage	Fog/toner Preservation of the environment scattering
16	27	C	carbon black (R-300, Cabot)	15.5	0	0	0/0
17	30	E	ditto	12.1	0	0	0/0
18	5	A	C.I. Pigment Red 122	10.5	0	0	0/0
19	7	A	C.I. Pigment Blue 15	10.8	0	0	0/0

TABLE 3

Compa- rative Example	Compound (A)	Inorganic pigment (B)	(A):(B) Resin	Colorant	Charge quantity ( $\mu\text{C/g}$ )	Rise of charging	Evaluation of toner		
							Image quality		
							Initial stage	After 50,000 copies environment	Fog/toner scattering
3	(5)	calcium sulfate	30:70	A carbon black (#44, Mitsubishi Kasei Corp.)	9.0	x	0	x	x/x
4	(7)	calcium carbonate*	10:100	A ditto	12.0	x	x	x	x/x
5	(10)	calcium carbonate	10:90	A ditto	8.0	x	x	x	x/x
6	(11)	$\text{CaCO}_3\text{:Al(OH)}_3$ (1:1)	50:50	A carbon black (R-300, Cabot)	9.0	x	x	x	x/x
7	(12)	magnesium carbonate	40:60	C ditto	12.5	x	0	x	x/x
8	(14)	$\text{CaCO}_3\text{:Al(OH)}_3$ (1:1)	25:75	C ditto	13.0	x	0	x	x/x
9	(18)	calcium silicate	100:10	C carbon black (ELFTEX-8, Cabot)	9.8	x	x	x	x/x
10	(18)	ditto	ditto	E ditto	9.0	x	0	x	x/x
11	(19)	$\text{CaCO}_3\text{:Al(OH)}_3$ (1:1)	80:20	A carbon black (#44, Mitsubishi Kasei Corp.)	10.6	x	x	x	x/x

TABLE 3 (cont'd)

Compa- rative Example	Compound (A)	Inorganic pigment (B)	(A):(B) Resin	Colorant	Charge quantity ( $\mu\text{C/g}$ )	Rise of charging	Evaluation of toner		
							Image quality	After Preservation of the environment	Fog/toner scattering
							Initial stage	50,000 copies	
12	(21)	aluminum silicate	50:50	A carbon black (#44, Mitsubishi Kasei Corp.)	9.0	x	x	x	x/x
13	(23)	barium carbonate	50:50	A carbon black (#44, Mitsubishi Kasei Corp.)	12.6	x	0	x	x/x
14	(24)	$\text{CaCO}_3\text{:Al(OH)}_3$ (1:1)	10:90	C carbon black (R-300, Cabot Corp.)	14.8	x	x	x	x/x
15	(26)	magnesium hydrogen- phosphate	100:10	E ditto	11.0	x	x	x	x/x
16	(2)	barium sulfate	25:75	A C.I. Pigment Red 122	9.6	x	0	x	x/x
17	(4)	calcium carbonate	100:10	A C.I. Pigment Blue 15	9.9	x	x	x	x/x

\* Calcium carbonate treated with titanium coupling agent

## EXAMPLE 20

There was dissolved 6.24 parts of N,N,N-tri-n-butyl-N-benzylammonium chloride in 100 parts of methanol. To the resulting solution, there was added 3.0 parts of calcium carbonate (1.5  $\mu\text{m}$ ). Subsequently,

an aqueous solution composed of 7.65 parts of sodium 1,7-dihydroxynaphthalene-3-sulfonate and 100 parts of water was added thereto. The mixture was stirred at 50 °C for 2 hours. The precipitated white precipitate was recovered by filtration, thoroughly washed with water and dried to obtain Composition 31 composed of the quaternary ammonium salt and calcium carbonate (75:25).

A toner was prepared in the same manner as in Example 1 except that Composition 31 was used in place of Composition 1. The tribo charge quantity of the toner was measured.

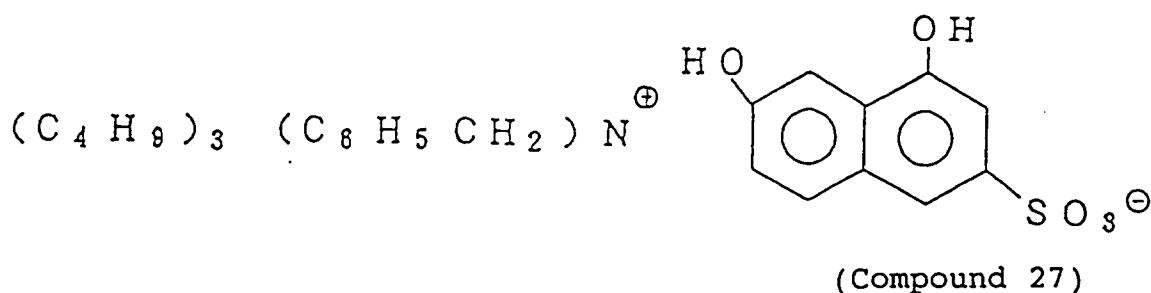
After stirring of the toner with an iron powder carrier for 30 seconds, one minute, 3 minutes, 5 minutes, 10 minutes, 30 minutes and 2 hours, the tribo charge quantities ( $\mu\text{C/g}$ ) were 3.0, 4.2, 7.0, 9.0, 9.1, 9.2 and 9.3, respectively. The value after 5 minutes was 96.8% of that after 2 hours. Accordingly, a rise of charging was good.

The toner was put into the development device, and continuous copying was carried out to make an image test. A good image was obtained at the initial stage of running. After obtaining 50,000 copies, the image quality was not changed, and neither toner scattering nor offset occurred.

Further, the continuous copying test was carried out under high temperature and humidity conditions at 35 °C and 85% RH and under low temperature and humidity conditions at 10 °C and 30% RH. An image quality substantially equal to that obtained by conducting copying under normal temperature and humidity conditions was obtained. Neither toner scattering nor offset occurred.

#### EXAMPLE 21

Quaternary ammonium salt:



There was dissolved 6.24 parts of N,N,N-tri-n-butyl-N-benzylammonium chloride in 100 parts of methanol. Subsequently, an aqueous solution composed of 7.65 parts of sodium 1,7-dihydroxynaphthalene-3-sulfonate and 100 parts of water was added thereto. The mixture was stirred at 50 °C for 2 hours. The resulting quaternary ammonium salt (Compound 27) was recovered by filtration, and the wet cake was dispersed in 100 parts of water with stirring at room temperature. To the dispersion, there was added 3.0 parts of the same calcium carbonate (1.5  $\mu\text{m}$ ) as that used in Example 20. The mixture was stirred overnight. The product was recovered by filtration, thoroughly washed with water and dried to obtain Composition 32 having the same composition ratio as that of Composition 31.

A toner was prepared in the same manner as in Example 1 except that Composition 32 was used in place of Composition 1. The tribo charge quantity of the toner was measured.

After stirring of the toner with an iron powder carrier for 30 seconds, one minute, 3 minutes, 5 minutes, 10 minutes, 30 minutes and 2 hours, the tribo charge quantities ( $\mu\text{C/g}$ ) were 2.8, 4.0, 6.3, 8.7, 9.0, 9.1 and 9.2, respectively. The value after 5 minutes was 94.6% of that after 2 hours. Accordingly, a rise of charging was good.

The toner was put into a development device, and continuous copying was carried out to make image test. A good image was obtained at the initial stage of running. After obtaining 50,000 copies, the image quality was not charged, and neither toner scattering nor offset occurred.

Further, the continuous copying test was carried out under high temperature and humidity conditions at 35 °C and 85% RH and under low temperature and humidity conditions at 10 °C and 30% RH. An image quality substantially equal to that obtained by conducting copying under normal temperature and humidity conditions was obtained. Neither toner scattering nor offset occurred.

EXAMPLE 22

The quaternary ammonium salt (Compound 27) synthesized in the same manner as in Example 22 was recovered by filtration, thoroughly washed with water and dried. Immediately after drying, the same calcium carbonate (1.5  $\mu\text{m}$ ) as that used in Example 20 was mixed with the salt. The mixture was pulverized in a pulverizer to obtain Composition 33 composed of the quaternary ammonium salt and calcium carbonate (75:25).

A toner was prepared in the same manner as in Example 1 except that Composition 33 was used in place of Composition 1. The tribo charge quantity of the toner was measured.

After stirring of the toner with an iron powder carrier for 30 seconds, one minute, 3 minutes, 5 minutes, 10 minutes, 30 minutes and 2 hours, the tribo charge quantity ( $\mu\text{C/g}$ ) were 2.6, 3.8, 6.0, 8.5, 8.8, 8.9 and 9.3, respectively.

The value after 5 minutes was 91.4% of that after 2 hours. Accordingly, a rise of charging was good.

The toner was put into a development device, and continuous copying was carried out to make an image test. A good image was obtained at the initial stage of running. After obtaining 50,000 copies, the image quality was not changed, and neither toner scattering nor offset occurred.

Further, the continuous copying test was carried out under high temperature and humidity conditions at 35°C and 85% RH and under low temperature and humidity conditions at 10°C and 30% RH. An image quality substantially equal to that obtained by conducting copying under normal temperature and humidity conditions was obtained. Neither toner scattering nor offset occurred.

COMPARATIVE EXAMPLE 18

One part of the quaternary ammonium salt (Compound 27) synthesized and dried in the same manner as in Example 21 was used, and a toner was prepared in the same manner as in Example 1 except that aluminum hydroxide was omitted. The tribo charge quantity of the toner was measured.

After stirring of toner with an iron powder carrier for 30 seconds, one minute, 3 minutes, 5 minutes, 10 minutes and 2 hours, the tribo charge quantities ( $\mu\text{C/g}$ ) were 2.0, 3.1, 5.2, 5.8, 7.0, 8.0 and 9.0, respectively. The value after 5 minutes was 64.4% of that after 2 hours. Hence, a rise of charging was poor.

An image test was made in the same manner as in Example 1. A clear image which was not fogged was obtained at the initial stage of running. However, after obtaining about 1,000 copies, an image which was fogged and not clear was obtained.

COMPARATIVE EXAMPLE 19

A toner was prepared in the same manner as in Example 1 by using the quaternary ammonium salt (Compound 27) synthesized and dried in the same manner as in Example 21 and the following composition.

Styrene-n-butyl methacrylate copolymer resin (Himer SBM-73F manufactured by Sanyo Kasei KK)	88 parts
Low-molecular polypropylene (VISCOL 550-P manufactured by Sanyo Kasei KK)	5 parts
Carbon black (#44 manufactured by Mitsubishi Kasei Corporation)	5 parts
Quaternary ammonium salt (Compound 27)	1 part
Calcium carbonate (1.5 $\mu\text{m}$ )	1 part

The tribo charge quantity of the resulting toner was measured. After stirring of the toner with an iron powder carrier for 30 seconds, one minute, 3 minutes, 5 minutes, 10 minutes and 2 hours, the tribo charge quantities ( $\mu\text{C/g}$ ) were 2.1, 3.3, 5.3, 6.0, 7.7, 8.0 and 9.2, respectively. The value after 5 minutes was 65.2% of that after 2 hours. Hence, the toner had a poor rise of charging.

In the same manner as in Example 1, an image test was carried out. A clear image which was not fogged was obtained at the initial stage of running. However, after obtaining about 1,000 copies, an image which was fogged and not clear was obtained.

EXAMPLES 23 TO 46, AND COMPARATIVE EXAMPLES 20 TO 43

Compositions 34 to 68 indicated in Table 4 were prepared by adding inorganic pigments during the course of the preparation of the quaternary ammonium salt in the same manner as in Example 20, and used in Examples 23 to 46 shown in Table 5. Compositions were prepared in the same manner as in Comparative Example 19 by using the quaternary ammonium salt synthesized and dried in the same manner as in Example 21, and used in Comparative Examples 20 to 43 shown in Table 6. The results are shown in Tables 5 to 6.

Binder resins, charge quantity-measuring method and the criterion used in the Tables are as follows.

Binder resins used in the preparation of toners:

- A: styrene-acrylic acid copolymer (Himer SBM-73 manufactured by Sanyo Kasei KK)
- B: Styrene-acrylic acid copolymer (Himer TB-1000 manufactured by Sanyo Kasei KK)
- C: Polyester (HP-313 manufactured by Nippon Gosei Kagaku KK)
- D: Polyester (HP-320 manufactured by Nippon Gosei Kagaku KK)
- E: Polyester (average molecular weight: 1500)
- Charge quantity: Value measured after stirring for 2 hours.
- Criterion: The mark ○ means that there is practically no problem.  
The mark X means that there is practically a problem.



TABLE 4

Composition No.	Quaternary ammonium salt (A)	Compound (No.)	Inorganic pigment (B)	Composition ratio (by weight) (A):(B)
34	$(C_{18}H_{33})_2(CH_3)_2N^+ \cdot SO_3^-$ 	(28)	zinc silicate	20:80
35	$(C_{18}H_{37})(C_{14}H_{29})(CH_3)_2N^+ \cdot SO_3^-$ 	(29)	calcium sulfate	70:30
36	$(C_{18}H_{37})_2(CH_3)_2N^+ \cdot SO_3^-$ 	(30)	barium sulfate	50:50
37	$(C_{18}H_{37})_3NCH_2 \cdot SO_3^-$ 	(31)	aluminum silicate	80:20
38	$(CH_3OC_6H_{16})(CH_3)_3N^+ \cdot 1/2 SO_3^-$ 	(32)	calcium carbonate	10:100
39	$(C_{18}H_{37})_2(CH_3)_2N^+ \cdot SO_3^-$ 	(33)	calcium carbonate	10:100
40	$(C_{18}H_{37})_2(CH_3)_2N^+ \cdot SO_3^-$ 	(34)	calcium sulfate	20:80

TABLE 4 (cont'd)


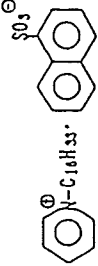
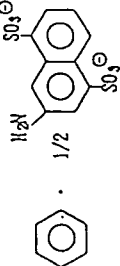
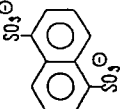
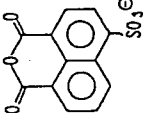
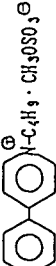
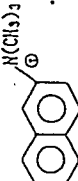

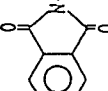
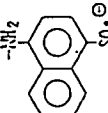
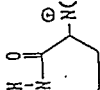


Composition No.	Quaternary ammonium salt (A)	Compound (No.)	Inorganic pigment (B)	Composition ratio (by weight) (A):(B)
41	$(C_{11}H_{23}CONH(CH_2)_3)^+ (CH_3)_2NCH_2-$  $-SO_3^-$	(35)	aluminum hydroxide	50:50
42	 $-C_{10}H_{13}^+$ $-SO_3^-$	(36)	mixture (1:1) of $CaCO_3$ and $Al(OH)_3$	30:70
43	$(C_{10}H_{17})^+ (CH_3)_2NCH_2-$  $-SO_3^-$ $\cdot 1/2$  $-SO_3^-$	(37)	magnesium hydroxide	10:90
44	$(C_{14}H_{29})^+ (CH_3)_2N \cdot$  $-SO_3^-$	(38)	aluminum hydroxide	10:90
45	$(C_{14}H_{29})^+ (CH_3)_2N \cdot$  $-C_4H_9 \cdot CH_3SO_3^-$	(39)	magnesium hydrogen-phosphate	70:30
46	 $-N(CH_3)_3^+$ $\cdot$  $-SO_3^-$	(40)	barium carbonate	90:10
47	 $-N(CH_2)_3(CH_3)_3N^+$ $\cdot$  $-NH_2$ $-SO_3^-$	(41)	calcium sulfate	75:25
48	 $-N(CH_3)_2 (CH_2)_2$  $-CH_3$  $-SO_3^-$	(42)	calcium carbonate	80:20

TABLE 4 (cont'd)

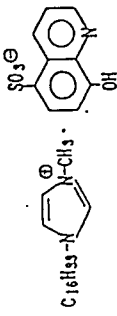
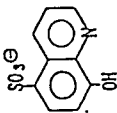
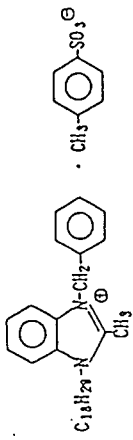
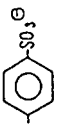
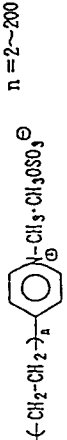
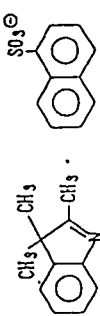
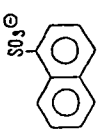
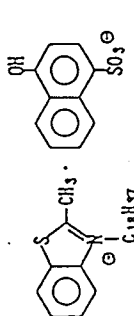
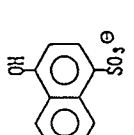
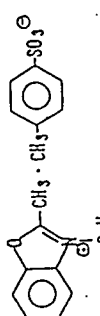
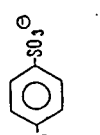


Composition No.	Quaternary ammonium salt (A)	Compound (No.)	Inorganic pigment (B)	Composition ratio (by weight) (A):(B)
49	 C <sub>16</sub> H <sub>33</sub> -N <sup>+</sup> · 	(43)	magnesium hydroxide	30:70
50	 C <sub>16</sub> H <sub>29</sub> -N <sup>+</sup> · 	(44)	barium carbonate	50:50
51	 -(CH <sub>2</sub> -CH <sub>2</sub> ) <sub>n</sub> -N <sup>+</sup> · C <sub>16</sub> H <sub>33</sub> SO <sub>3</sub> <sup>-</sup> n = 2~200 average MW 1500	(45)	calcium carbonate	25:75
52	 C <sub>16</sub> H <sub>33</sub> · 	(46)	mixture (1:1) of BaSO <sub>4</sub> and CaCO <sub>3</sub>	50:50
53	 C <sub>16</sub> H <sub>33</sub> · 	(47)	calcium carbonate	25:75
54	 C <sub>4</sub> H <sub>9</sub> · 	(48)	calcium carbonate	50:50
55	 C <sub>16</sub> H <sub>33</sub> · 	(49)	mixture (1:1) of CaCO <sub>3</sub> and Al(OH) <sub>3</sub>	60:40

TABLE 4 (cont'd)

Composition No.	Quaternary ammonium salt (A)	Compound (No.)	Inorganic pigment (B)	Composition ratio (by weight) (A):(B)
56		(50)	aluminum silicate	10:100
57		(51)	calcium carbonate	50:50
58		(52)	mixture (1:1) of BaSO <sub>4</sub> and Al(OH) <sub>3</sub>	40:60
59		(53)	aluminum hydroxide	50:50
60		(54)	barium sulfate	70:30
61		(55)	mixture (1:1) of BaSO <sub>4</sub> and Al(OH) <sub>3</sub>	20:80
62		(56)	mixture (1:1) of BaSO <sub>4</sub> and Al(OH) <sub>3</sub>	20:80

TABLE 4 (cont'd)

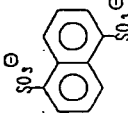
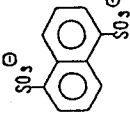
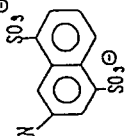
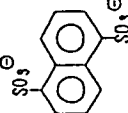
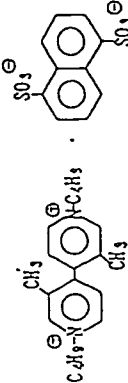
Composition No.	Quaternary ammonium salt (A)	Compound (No.)	Inorganic pigment (B)	Composition ratio (by weight) (A):(B)
63	$(C_{18}H_{37})^+(CH_3)_2NH \cdot 1/2$ 	(57)	calcium carbonate	50:50
64	$(CH_3)_2N^+-CH_2CH_2-N^+(CH_3)_2 \cdot$ 	(58)	calcium carbonate	25:75
65	$(CH_3)_2N^+-CH_2CH_2-N^+(CH_3)_2 \cdot$ 	(59)	aluminum hydroxide	25:75
66	$(CH_3)_3N^+-CH_2CH_2-N^+(CH_3)_3 \cdot$ 	(60)	mixture (1:1) of CaCO <sub>3</sub> and Al(OH) <sub>3</sub>	50:50
67	$(C_{18}H_{37})_2(CH_3)_2N^+ \cdot CH_3OSO_3^-$	(61)	mixture (1:1) of CaCO <sub>3</sub> and Al(OH) <sub>3</sub>	50:50
68		(62)	calcium carbonate	40:60

TABLE 5

Example	Composition No.	Resin	Colorant	Evaluation of toner					
				Charge quantity ( $\mu\text{C/g}$ )	Rise of charging	Image quality		Preservation of the environment	Fog/toner scattering
						Initial stage	After 50,000 copies		
23	34	A	carbon black (R-300, Cabot Corp.)	9.1	0	0	0	0	0/0
24	35	E	ditto	8.3	0	0	0	0	0/0
25	38	A	ditto	12.0	0	0	0	0	0/0
26	39	A	ditto	10.6	0	0	0	0	0/0
27	40	C	carbon black (ELFTEX-8, Cabot Corp.)	13.2	0	0	0	0	0/0
28	42	C	ditto	11.2	0	0	0	0	0/0
29	43	C	carbon black (#44, Mitsubishi Kasei Corp.)	10.0	0	0	0	0	0/0
30	44	E	C.I. Pigment Red 122	14.7	0	0	0	0	0/0
31	45	E	C.I. Pigment Red 122	12.6	0	0	0	0	0/0
32	46	A	C.I. Pigment Blue 15	13.0	0	0	0	0	0/0
33	49	A	C.I. Pigment Yellow 16	15.4	0	0	0	0	0/0

TABLE 5 (cont'd)

Example	Composition No.	Resin	Colorant	Evaluation of toner					
				Charge quantity ( $\mu\text{C/g}$ )	Rise of charging	Image quality		Preservation of the environment	Fog/toner scattering
						Initial stage	After 50,000 copies		
34	50	A	carbon black (R-300, Cabot Corp.)	11.1	0	0	0	0	0/0
35	54	C	ditto	9.8	0	0	0	0	0/0
36	56	C	ditto	11.8	0	0	0	0	0/0
37	57	B	carbon black (ELFTEX-8, Cabot Corp.)	10.2	0	0	0	0	0/0
38	58	B	carbon black (R-300, Cabot Corp.)	11.8	0	0	0	0	0/0
39	61	C	magnetic powder	8.0	0	0	0	0	0/0
40	59	C	ditto	9.0	0	0	0	0	0/0
41	60	C	C.I. Pigment Blue 15	6.2	0	0	0	0	0/0
42	62	A	carbon black (#44, Mitsubishi Kasei Corp.)	14.0	0	0	0	0	0/0
43	63	A	ditto	13.1	0	0	0	0	0/0
44	64	C	ditto	15.5	0	0	0	0	0/0
45	65	C	C.I. Pigment Red 122	12.0	0	0	0	0	0/0
46	50	A	carbon black (#44, Mitsubishi Kasei Corp.)	11.2	0	0	0	0	0/0

TABLE 6

Compa- rative Example	Compound (A)	Inorganic pigment (B)	(A):(B) Resin	Colorant	Charge quantity ( $\mu\text{C/g}$ )	Rise of charging	Evaluation of toner		
							Image quality		Fog/toner scattering
							Initial stage	After Preservation 50,000 copies environment	
20	(28)	zinc silicate	20:80	A carbon black (R-300, Cabot Corp.)	8.5	x	0	x	x/x
21	(29)	calcium sulfate	70:30	E ditto	8.0	x	x	x	x/x
22	(32)	calcium carbonate	10:100	A ditto	11.0	x	0	x	x/x
23	(33)	calcium carbonate	10:100	A ditto	9.5	x	x	x	x/x
24	(34)	calcium sulfate	20:80	C carbon black (ELFTEX-8, Cabot Corp.)	11.0	x	x	x	x/x
25	(36)	$\text{CaCO}_3\text{:Al(OH)}_3$ (1:1)	30:70	C ditto	10.8	x	x	x	x/x
26	(37)	magnesium hydroxide	10:90	C carbon black (#40, Mitsubishi Kasei Corp.)	9.0	x	x	x	x/x
27	(38)	aluminum hydroxide	10:90	E C.I. Pigment Red 122	12.0	x	x	x	x/x



TABLE 6 (cont'd.)

Compa- rative Example	Compound (A)	Inorganic pigment (B)	(A):(B) Resin	Colorant	Charge quantity ( $\mu\text{C/g}$ )	Rise of charging	Evaluation of toner		
							Image quality	After Preservation	Fog/toner
							Initial	50,000	of the
							stage	copies	environment
									scattering
28	(39)	magnesium hydrogen- phosphate	70:30	E C.I. Pigment Red 122	12.3	x	x	x	x
29	(41)	calcium sulfate	75:25	A C.I. Pigment Blue 15	12.0	x	x	x	x/x
30	(44)	barium sulfate	50:50	A C.I. Pigment Yellow 16	15.0	x	x	x	x/x
31	(45)	calcium carbodate	40:60	A carbon black (R-300, Cabot Corp.)	10.8	x	x	x	x/x
32	(49)	$\text{CaCO}_3:\text{Al}(\text{O})$ $\text{H})_3$ (1:1)	60:40	C ditto	9.0	x	O	x	x/x
33	(51)	calcium carbonate	50:50	C ditto	10.2	x	O	x	x/x
34	(52)	$\text{BaSO}_4:\text{Al}(\text{O})$ $\text{H})_3$ (1:1)	40:60	B carbon black (ELFTEX-8, Cabot Corp.)	9.3	x	x	x	x/x
35	(53)	aluminum hydroxide	50:50	B carbon black (R-300, Cabot Corp.)	10.0	x	x	x	x/x

TABLE 6 (cont'd)

Compa- rative Example	Compound (A)	Inorganic pigment (B)	(A):(B) Resin	Colorant	Charge quantity ( $\mu\text{C/g}$ )	Rise of charging	Evaluation of toner		
							Image quality	After Preservation of the environment	Fog/toner scattering
36	(56)	BaSO <sub>4</sub> :Al(OH) <sub>3</sub> (1:1)	20:80	C magnetic powder	7.1	x	x	x	x/x
37	(54)	BaSO <sub>4</sub> Barium sulfate	70:30	C ditto	8.1	x	x	x	x/x
38	(55)	BaSO <sub>4</sub> :Al(OH) <sub>3</sub> (1:1)	20:80	C C.I. Pigment Blue 15	5.5	x	O	x	x/x
39	(57)	calcium carbonate	50:50	A carbon black (#44, Mitsubishi Kasei Corp.)	12.0	x	O	x	x/x
40	(58)	calcium carbonate	25:75	A ditto	11.1	x	x	x	x/x
41	(59)	aluminum hydroxide	25:75	C ditto	13.0	x	x	x	x/x
42	(60)	CaCO <sub>3</sub> :Al(OH) <sub>3</sub> (1:1)	50:50	C C.I. Pigment Red 122	9.8	x	x	x	x/x
43	(45)	calcium carbonate	25:75	A carbon black (#44, Mitsubishi Kasei Corp.)	10.6	x	x	x	x/x

## EXAMPLE 47

There was dissolved 20.0 parts of N,N-dimethyl-N,N-ditetradecylammonium chloride in 100 parts of methanol. To the resulting solution, there was added 8.2 parts of aluminum hydroxide (2  $\mu\text{m}$ ). Subse-

quently, a solution composed of 14.4 parts of sodium tetraphenylborate and 100 parts of methanol was added thereto. The mixture was stirred at 30 °C. The precipitated white precipitate was recovered by filtration, thoroughly washed with water and dried to obtain Composition 69 composed of the quaternary ammonium salt and aluminum hydroxide (80:20).

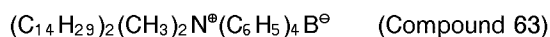
5 A toner was prepared in the same manner as in Example 1 except that Composition 69 was used in place of Composition 1. The tribo charge quantity of the toner was measured. After stirring time for 30 seconds, one minute, 3 minutes, 5 minutes, 10 minutes, 30 minutes and 2 hours, the tribo charge quantities ( $\mu\text{C/g}$ ) were 2.5, 4.0, 6.1, 8.8, 9.0, 9.2 and 9.3, respectively. The value after 5 minutes was 94.6% of that after 2 hours. Hence, a rise of charging was good.

10 The toner was put into a development device, and continuous copying was carried out to make an image test. A good image was obtained at the initial stage of running. After obtaining 50,000 copies, the image quality was not changed, and neither toner scattering nor offset occurred.

Further, the continuous copying test was carried out under high temperature and humidity conditions at 35 °C and 85% RH and under low temperature and humidity conditions at 10 °C and 30% RH. An image quality substantially equal to that obtained by conducting copying under normal temperature and humidity conditions was obtained. Neither toner scattering nor offset occurred.

#### EXAMPLE 48

20 Quaternary ammonium salt:



25 There was dissolved 20.0 parts of N,N-dimethyl-N,N-ditetradecylammonium chloride in 100 parts of aqueous methanol. To the resulting solution, there was added a solution composed of 14.4 part of sodium tetraphenylborate and 100 parts of methanol. The mixture was stirred at 30 °C. The resulting quaternary ammonium salt (Compound 63) was recovered by filtration.

30 The wet cake was dispersed in 100 parts of water with stirring at room temperature. Subsequently, 8.2 parts of the same aluminum hydroxide (2  $\mu\text{m}$ ) as that used in Example 47 was added thereto. The mixture was stirred overnight. The product was recovered by filtration, thoroughly washed with water and dried to obtain Composition 70 composed of the quaternary ammonium salt (Compound 63) and aluminum hydroxide (80:20).

35 A toner was prepared in the same manner as in Example 1 except that Composition 70 was used in place of Composition 1. The tribo charge quantity of the toner was measured. After stirring of the toner with an iron powder carrier for 30 seconds, one minute, 3 minutes, 5 minutes, 10 minutes, 30 minutes and 2 hours, the tribo charge quantities ( $\mu\text{C/g}$ ) were 2.3, 4.0, 5.4, 8.6, 8.9, 9.0 and 9.3, respectively. The tribo charge quantity after stirring for 5 minutes was 92.5% of that after 2 hours. Hence, there was obtained a toner having a good rise of charging in a short period of time.

40 The toner was put into a development device, and continuous copying was carried out to make an image test. A good image was obtained at the initial stage of running. After obtaining 50,000 copies, the image quality was not changed, and neither toner scattering nor offset occurred. Further, the continuous copying test was carried out under high temperature and humidity conditions and under low temperature and humidity conditions. An image of good quality was obtained without being affected by environmental conditions.

#### EXAMPLE 49

45 The quaternary ammonium salt (Compound 63) synthesized in the same manner as in Example 48 was recovered by filtration and dried. Immediately after drying, the same aluminum hydroxide (2  $\mu\text{m}$ ) as that used in Example 47 was mixed with the salt. The mixture was pulverized in a pulverizer to obtain Composition 71 composed of the quaternary ammonium salt and aluminum hydroxide (80:20).

55 A toner was prepared in the same manner as in Example 1 except that Composition 71 was used in place of Composition 1. The tribo charge quantity of the toner was measured. After stirring of the toner with an iron powder carrier for 30 seconds, one minute, 3 minutes, 5 minutes, 10 minutes, 30 minutes and 2 hours, the tribo charge quantities ( $\mu\text{C/g}$ ) were 2.4, 4.1, 5.6, 8.4, 8.8, 9.0 and 9.2, respectively. The value measured after stirring for 5 minutes was 91.3% of that after 2 hours. Hence, there was obtained a toner having a good rise of charging in a short period of time.

The toner was put into a development device, and continuous copying was carried out to make an image test. A good image was obtained at the initial stage of running. After obtaining 50,000 copies, the image quality was not changed, and neither toner scattering nor offset occurred.

Further, the continuous copying test was carried out under high temperature and humidity conditions at 35 °C and 85% RH and under low temperature and humidity conditions at 10 °C and 30% RH. An image quality substantially equal to that obtained by conducting copying under normal temperature and humidity conditions was obtained. Neither toner scattering nor offset occurred.

#### COMPARATIVE EXAMPLE 44

One part of the quaternary ammonium salt (Compound 63) synthesized and dried in the same manner as in Example 48 was used, and a toner was prepared in the same manner as in Example 1 except that aluminum hydroxide was omitted. The tribo charge quantity of the toner was measured. After stirring of the resulting developer for 30 seconds, one minute, 3 minutes, 5 minutes, 10 minutes, 30 minutes and 2 hours, the tribo charge quantities ( $\mu\text{C/g}$ ) were 1.8, 3.0, 4.4, 6.0, 7.6, 8.6 and 9.4, respectively. The tribo charge quantity after stirring for 5 minutes was 63.8% of that after 2 hours. Hence, a rise of charging was very poor.

An image test was carried out in the same manner as in Example 1. A clear image which was not fogged was obtained at the initial stage of running. However, after obtaining about 1,000 copies, an image which was fogged and not clear was obtained.

#### COMPARATIVE EXAMPLE 45

A toner was prepared by using the quaternary ammonium salt (Compound 63) synthesized and dried in the same manner as in Example 48 and the following composition in the same manner as in Example 1.

Styrene-n-butyl methacrylate copolymer resin (Himer SBM-73F manufactured by Sanyo Kasei KK)	88 parts
Low-molecular polypropylene (VISCOL 550-P manufactured by Sanyo Kasei KK)	5 parts
Carbon black (#44 manufactured by Mitsubishi Kasei Corporation)	5 parts
Quaternary ammonium salt (Compound 63)	1 part
Aluminum hydroxide (2 $\mu\text{m}$ )	1 part

A developer was prepared by using the resulting toner in the same manner as in Example 1. After stirring of the toner with an iron powder carrier for 30 seconds, one minute, 3 minutes, 10 minutes, 30 minutes and 2 hours, the tribo charge quantities ( $\mu\text{C/g}$ ) were 1.9, 3.1, 4.8, 6.5, 7.8, 8.7 and 9.5, respectively. The tribo charge quantity after stirring for 5 minutes was 68.4% of that after 2 hours. Hence, a rise of charging was poor.

An image test was carried out in the same manner as in Example 1. A good image which was not fogged was obtained at the initial stage of running. However, after obtaining about 1,000 copies, an image which was fogged and not clear was obtained.

#### EXAMPLE 50

Composition 72 was prepared in the same manner as in Example 47 except that aluminum hydroxide (30  $\mu\text{m}$ ) was used in place of aluminum hydroxide (2  $\mu\text{m}$ ). A toner was prepared in the same manner as in Example 1 except that Composition 72 was used in place of Composition 1. The tribo charge quantity of the toner was measured. After the mixing of the toner with an iron powder carrier for 30 seconds, one minute, 3 minutes, 5 minutes, 10 minutes, 30 minutes and 2 hours, the tribo charge quantities ( $\mu\text{C/g}$ ) were 2.6, 4.3, 6.3, 8.9, 9.0, 9.3 and 9.3, respectively. The value after stirring for 5 minutes was 95.7% of that after 2 hours. Hence, a rise of charging was good.

The toner was put into a development device, and continuous copying was carried out to make an image test. A good image was obtained at the initial stage of running. After obtaining 50,000 copies, the image quality was not changed, and neither toner scattering nor offset occurred.

Further, the continuous copying test was carried out under high temperature and humidity conditions at 35 °C and 85% RH and under low temperature and humidity conditions at 10 °C and 30% RH. An image quality substantially equal to that obtained by conducting copying under normal temperature and humidity conditions was obtained. Neither toner scattering nor offset occurred.

#### EXAMPLE 51

Quaternary ammonium salt:

$(C_{14}H_{29})_2(CH_3)_2N^{\oplus}Br^{\ominus}$  (Compound 64)

There were dissolved 12.5 parts of N,N-dimethyl-N-tetradecylamine and 20.0 parts of tetradecyl bromide in 100 parts of methanol. To the resulting solution, there was added 18.0 parts of calcium carbonate (1.5  $\mu m$ ). The mixture was stirred at 50 °C. The precipitated white precipitate was recovered by filtration and dried to obtain Composition 73 composed of the quaternary ammonium salt and calcium carbonate (50:50).

A toner was prepared in the same manner as in Example 1 except that Composition 73 was used in place of Composition 1. The tribo charge quantity of the toner was measured. After stirring for 30 seconds, one minute, 3 minutes, 5 minutes, 10 minutes, 30 minutes and 2 hours, the tribo charge quantities ( $\mu C/g$ ) were 3.3, 5.3, 7.2, 9.9, 10.1, 10.3 and 10.4, respectively. The value after stirring for 5 minutes was 95.2% of that after 2 hours. Hence, a rise of charging was good.

The toner was put into a development device, and continuous copying was carried out to make an image test. A good image was obtained at the initial stage of running. After obtaining 50,000 copies, the image quality was not changed, and neither toner scattering nor offset occurred.

Further, the continuous copying test was carried out under high temperature and humidity conditions at 35 °C and 85% RH and under low temperature and humidity conditions at 10 °C and 30% RH. An image quality substantially equal to that obtained by conducting copying under normal temperature and humidity conditions was obtained. Neither toner scattering nor offset occurred.

#### EXAMPLE 52

There were dissolved 12.5 parts of N,N-dimethyl-N-tetradecylamine and 20.0 parts of tetradecyl bromide in 100 parts of methanol. The mixture was stirred at 50 °C. The formed quaternary ammonium salt (Compound 64) was recovered by filtration.

The wet cake was dispersed in 60 parts of water with stirring at 10 °C. Subsequently, 19 parts of the same calcium carbonate (1.5  $\mu m$ ) as that used in Example 51 was added thereto. The mixture was stirred overnight. The product was recovered by filtration, washed with water and dried to obtain Composition 74 composed of the quaternary ammonium salt (Compound 64) and calcium carbonate (50:50).

A toner was prepared in the same manner as in Example 1 except that Composition 74 was used in place of Composition 1. The tribo charge quantity of the toner was measured. After stirring the toner with an iron powder carrier for 30 seconds, one minute, 3 minutes, 5 minutes, 10 minutes, 30 minutes and 2 hours, the tribo charge quantities ( $\mu C/g$ ) were 3.0, 5.0, 7.1, 9.5, 9.9, 10.2 and 10.3, respectively. The tribo charge quantity after stirring for 5 minutes was 92.2% of that after 2 hours. Hence, there was obtained a toner having a good rise of charging in a short period of time.

The toner was put into a development device, and continuous copying was carried out to make an image test. A good image was obtained at the initial stage of running. After obtaining 50,000 copies, the image quality was not changed, and neither toner scattering nor offset occurred. Further, the continuous copying test was carried out under high temperature and humidity conditions and under low temperature and humidity conditions. An image of good quality was obtained without being affected by environmental conditions.

#### COMPARATIVE EXAMPLE 46

A toner was prepared in the same manner as in Example 1 except that 1.0 part of the quaternary ammonium salt (Compound 64) synthesized and dried in the same manner as in Example 52 was used, water was not used and aluminum hydroxide was omitted. The tribo charge quantity of the toner was measured. After stirring the resulting developer for 30 seconds, one minute, 3 minutes, 5 minutes, 10 minutes, 30 minutes and 2 hours, the tribo charge quantities ( $\mu C/g$ ) were 1.8, 3.0, 4.2, 5.3, 6.0, 6.8 and 7.3,

respectively. The tribo charge quantity after stirring for 5 minutes was 72.6% of that after 2 hours. Hence, the toner had a very poor rise of charging.

An image test was carried out in the same manner as in Example 1. A clear image which was not fogged was obtained at the initial stage of running. However, after obtaining about 1,000 copies, an image which was fogged and not clear was obtained.

#### EXAMPLES 53 TO 62 AND COMPARATIVE EXAMPLES 47 TO 56

Compositions 75 to 87 containing the quaternary ammonium salts indicated in Table 7 were prepared in the same manner as in Example 47 and used in Examples 53 to 62 shown in Table 8. Further, the quaternary ammonium salts were used in Comparative Examples 47 to 56 in the same manner as in Comparative Example 45. The results are shown in Tables 8 and 9.

Binder resins, charge quantity-measuring method and the criterion of the evaluation of each item used in Tables 8 and 9 are as follows.

Binder resins used in the preparation of toners:

- A: styrene-acrylic resin copolymer (Himer SBM-73 manufactured by Sanyo Kasei KK)
- B: Styrene-acrylic resin copolymer (Himer TB-1000 manufactured by Sanyo Kasei KK)
- C: Polyester (HP-313 manufactured by Nippon Gosei Kagaku KK)
- D: Polyester (HP-320 manufactured by Nippon Gosei Kagaku KK)
- E: Polystyrene (average molecular weight: 1500)
- Charge quantity: Value measured after stirring for 2 hours.
- Criterion: The mark ○ means that there is practically no problem.  
The mark X means that there is practically a problem.

TABLE 7

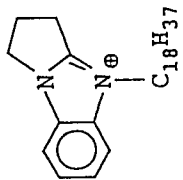
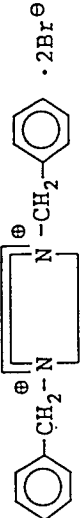
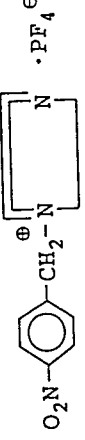
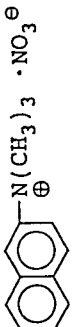
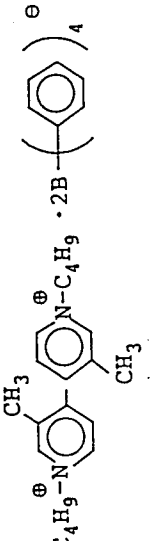

Composition No.	Quaternary ammonium salt (A)	Compound (No.)	Inorganic pigment (B)	Composition ratio (by weight) (A):(B)
75	$(C_{16}H_{33})_2(CH_3)(C_2H_4OH)N^+ \cdot ClO_4^-$	(65)	magnesium hydroxide	50:50
76	$(CH_3OC_8H_{16})(CH_3)_3N^+ \cdot I^-$	(66)	calcium sulfate	30:70
77	$\{C_{11}H_{23}CONH(CH_2)_3\}(CH_3)_2(CH_2C_6H_5)N^+ \cdot BF_4^-$	(67)	calcium sulfate	80:20
78	$C_{16}H_{33}-N^+ \langle \text{benzene ring} \rangle \cdot Cl^-$	(68)	calcium carbonate*	40:60
79	$(C_{18}H_{37})(C_6H_5CH_2)(CH_3)_2N^+ \cdot Cl^-$	(69)	magnesium carbonate	60:40
80	$(C_{18}H_{37})(C_6H_5CH_2)(CH_3)_2N^+ \cdot B-(C_6H_5)_4^-$	(70)	mixture (1:1) of $CaCO_3$ and $Al(OH)_3$	20:80
81	 $\cdot BF_4^-$	(71)	calcium carbonate	90:10
82	$(C_6H_5)_4N^+ \cdot BF_4^-$	(72)	calcium silicate	30:70

TABLE 7 (cont'd)

Composition No.	Quaternary ammonium salt (A)	Compound (No.)	Inorganic pigment (B)	Composition ratio (by weight) (A):(B)
83		(73)	zinc silicate	50:50
84		(74)	aluminum silicate	50:50
85		(75)	magnesium hydrogen-phosphate	10:90
86		(76)	aluminum hydroxide**	25:75
87		(77)	calcium carbonate	10:90

\* Surface was treated with titanate coupling agent.

\*\* Surface was treated with stearic acid.



TABLE 8

Example	Composition No.	Resin	Colorant	Evaluation of toner			
				Charge quantity ( $\mu\text{C/g}$ )	Rise of charging	Image quality Initial stage	Fog/toner scattering
53	75	A	carbon black (ELFTEX-8, Cabot Corp.)	10.3	0	0	0/0
54	78	A	ditto	13.5	0	0	0/0
55	79	B	ditto	10.0	0	0	0/0
56	80	C	carbon black (#44, Mitsubishi Kasei Corp.)	9.2	0	0	0/0
57	81	C	ditto	13.2	0	0	0/0
58	82	E	ditto	7.9	0	0	0/0
59	84	A	C.I. Pigment Red 122	12.1	0	0	0/0
60	85	A	ditto	9.6	0	0	0/0
61	86	B	C.I. Pigment Blue 15	7.0	0	0	0/0
62	77	E	magnetic powder	10.3	0	0	0/0

TABLE 9

Compa- rative Example	Compound (A)	Inorganic pigment (B)	(A):(B) Resin	Colorant	Evaluation of toner			
					Charge quantity ( $\mu\text{C/g}$ )	Rise of charging	Image quality After Preservation of the environment	Fog/toner scattering
47	(65)	magnesium hydroxide	50:50 A	carbon black (EPLTEX-8, Cabot)	9.6	x	x	x/x
48	(68)	calcium carbonate*	40:60 A	ditto	12.8	x	x	x/x
49	(69)	magnesium carbonate	60:40 B	ditto	9.0	x	x	x/x
50	(70)	mixture (1:1) of $\text{CaCO}_3$ and $\text{Al(OH)}_3$	20:80 C	carbon black (#44, Mitsubishi Kasei Corp.)	8.8	x	x	x/x
51	(71)	calcium carbonate	90:10 C	ditto	12.7	x	x	x/x
52	(72)	calcium silicate	30:70 E	ditto	7.1	x	x	x/x
53	(74)	zinc silicate	50:50 A	C.I. Pigment Red 122	11.8	x	x	x/x
54	(75)	dimagnesium phosphate	10:90 A	ditto	9.3	x	x	x/x
55	(76)	aluminum hydroxide**	25:75 B	C.I. Pigment Blue 15	6.5	x	x	x/x
56	(67)	calcium sulfate	80:20 E	magnetic powder	10.0	x	x	x/x

\* Surface was treated with titanate coupling agent.

\*\* Surface was treated with stearic acid.

It is seen from Examples and Comparative Examples that when the charge controlling agent composition according to the present invention, which comprises the quaternary ammonium salt and the inorganic pigment is used, the dispersibility of the quaternary ammonium salt having a charge controlling effect in the resin can be well-improved, and each toner particle has good charging characteristics, that is, a uniform charging level and excellent charge retention. As a result, the toner particles and the carrier can be

dispersed in each other in a short period of time, a rise of charging becomes rapider, and copying speed can be increased, and at the same time, the life of the toner can be prolonged and the toner is scarcely affected by the change of environmental conditions due to the change of temperature and humidity.

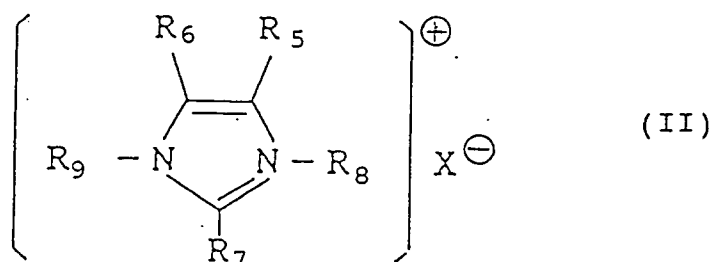
While the present invention has been described in detail and with reference to specific embodiments thereof, it is apparent to one skilled in the art that various changes and modifications can be made therein without departing from the spirit and the scope of the present invention.

## Claims

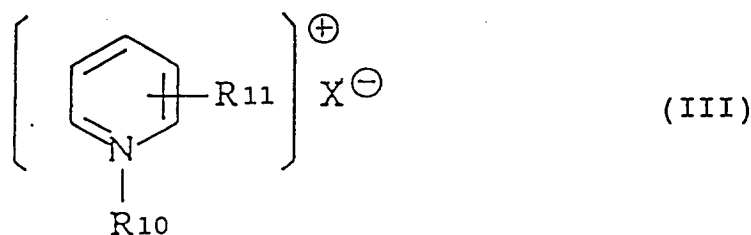
1. A charge controlling agent composition comprising a quaternary ammonium salt and an inorganic pigment selected from the group consisting of barium sulfate, magnesium hydroxide, aluminum hydroxide, calcium carbonate, magnesium carbonate, barium carbonate, calcium sulfate, zinc silicate, calcium silicate, aluminum silicate, magnesium silicate and magnesium hydrogenphosphate.
2. The charge controlling agent composition of claim 1, wherein the weight ratio of said quaternary ammonium salt to said inorganic pigment is from 0.5 to 99.5.
3. The charge controlling agent composition of claim 1, wherein said charge controlling agent composition is obtained by adding the inorganic pigment or inorganic compounds which form the inorganic pigment during the preparation of said quaternary ammonium salt, separating the resulting quaternary ammonium salt containing inorganic pigment, then drying the quaternary ammonium salt containing inorganic pigment.
4. The charge controlling agent composition of claim 1, wherein said charge controlling agent is prepared by mixing the quaternary ammonium salt and the inorganic pigment in the presence of a solvent, and then drying the resulting mixture.
5. The charge controlling agent composition of claim 1, wherein said charge controlling agent is prepared by mixing and stirring the quaternary ammonium salt and the inorganic pigment so as to uniformly adhere the inorganic pigment onto the particles of the quaternary ammonium salt.
6. The charge controlling agent composition of claim 1, wherein said quaternary ammonium salt is selected from the following compounds presented by the following formulas (I) to (VII):



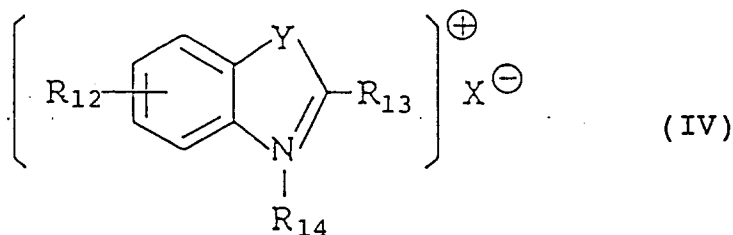
wherein  $R_1$ ,  $R_2$ ,  $R_3$  and  $R_4$  may be the same or different and each represents a hydrogen atom or an alkyl group containing 1 to 30 carbon atoms, an aralkyl group containing 7 to 30 carbon atoms or an aryl group containing 6 to 30 carbon atoms each of which may have one or more members selected from the group consisting of an amino group, an ether bond, a thioether bond, an alkoxy group, a hydroxy group, a carbonic acid amide group, a sulfonamide group, an urethane bond, a chloromethyl group, a nitro group, an aromatic group containing 6 to 30 carbon atoms and an aromatic heterocyclic group containing 6 to 30; and  $X^\ominus$  represents an anion;



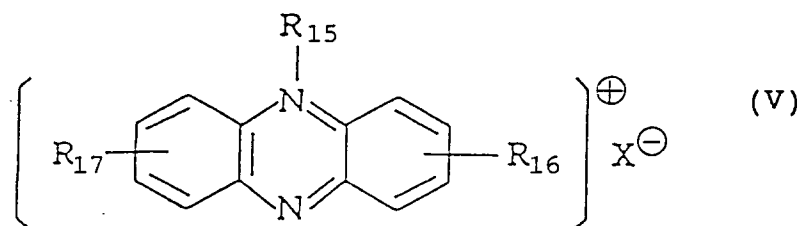
wherein  $\text{R}_5$ ,  $\text{R}_6$ ,  $\text{R}_7$ ,  $\text{R}_8$  and  $\text{R}_9$  may be the same or different and each represents a hydrogen atom or an alkyl group containing 1 to 30 carbon atoms, an aralkyl group containing 7 to 30 carbon atoms or an aryl group containing 6 to 30 carbon atoms each of which may have one or more members selected from the group consisting of an amino group, an ether bond, a thioether bond, an alkoxy group, a hydroxy group, a carbonic acid amide group, a sulfonamide group, an urethane bond, a chloromethyl group, a nitro group, an aromatic group containing 6 to 30 carbon atoms and an aromatic heterocyclic group containing 6 to 30 carbon atoms; and  $\text{X}^{\ominus}$  represents an anion; provided that  $\text{R}_5$  and  $\text{R}_6$  or  $\text{R}_7$  and  $\text{R}_8$  may be combined with each other to form an alicyclic or aromatic ring containing 6 to 30 carbon atoms;



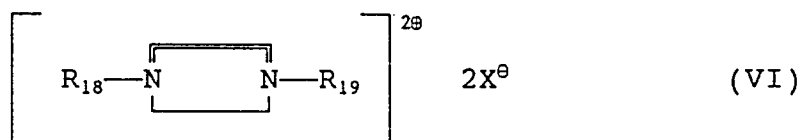
wherein  $\text{R}_{10}$  and  $\text{R}_{11}$  may be the same or different and each represents an alkyl group containing 1 to 30 carbon atoms, an aralkyl group containing 7 to 30 carbon atoms or an aryl group containing 6 to 30 carbon atoms each of which may have one or more members selected from the group consisting of an amino group, an ether bond, a thioether bond, an alkoxy group, a hydroxy group, a carbonic acid amide group, a sulfonamide group, an urethane bond, a chloromethyl group, a nitro group, an aromatic group containing 6 to 30 carbon atoms and an aromatic heterocyclic group containing 6 to 30 carbon atoms; and  $\text{X}^{\ominus}$  represents an anion; provided that  $\text{R}_{11}$  may represent a hydrogen atom;



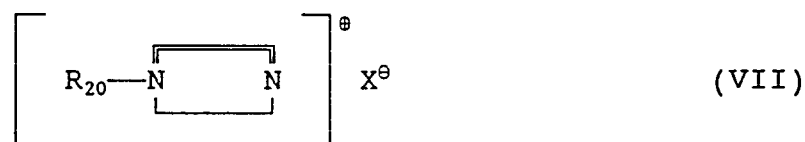
wherein  $\text{R}_{12}$ ,  $\text{R}_{13}$  and  $\text{R}_{14}$  may be the same or different and each represents an alkyl group containing 1 to 30 carbon atoms, an aralkyl group containing 7 to 30 carbon atoms or an aryl group containing 6 to 30 carbon atoms each of which may have one or more members selected from the group consisting of an amino group, an ether bond, a thioether bond, an alkoxy group, a hydroxy group, a carbonic acid amide group, a sulfonamide group, an urethane bond, a chloromethyl group, a nitro group, an aromatic group containing 6 to 30 carbon atoms and an aromatic heterocyclic group containing 6 to 30 carbon atoms; Y presents a carbon, oxygen or sulfur atom; and  $\text{X}^{\ominus}$  represents an anion; provided that  $\text{R}_{13}$  and  $\text{R}_{14}$  may be a hydrogen atom;



wherein  $\text{R}_{15}$ ,  $\text{R}_{16}$  and  $\text{R}_{17}$  may be the same or different and each represents an alkyl group containing 1 to 30 carbon atoms, an aralkyl group containing 7 to 30 carbon atoms or an aryl group containing 6 to 30 carbon atoms each of which may have one or more members selected from the group consisting of an amino group, an ether bond, a thioether bond, an alkoxy group, a hydroxy group, a carbonic acid amide group, a sulfonamide group, an urethane bond, a chloromethyl group, a nitro group, an aromatic group containing 6 to 30 carbon atoms and an aromatic heterocyclic group containing 6 to 30 carbon atoms; and  $\text{X}^{\ominus}$  represents an anion; provided that  $\text{R}_{16}$  and  $\text{R}_{17}$  may represent a hydrogen atom;



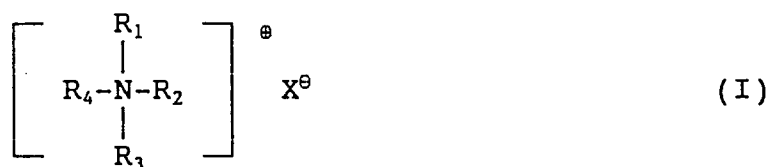
wherein  $\text{R}_{18}$  and  $\text{R}_{19}$  may be the same or different and each represents an alkyl group containing 1 to 30 carbon atoms, an aralkyl group containing 7 to 30 carbon atoms or an aryl group containing 6 to 30 carbon atoms which may have one or more members selected from the group consisting of an amino group, an ether bond, a thioether bond, an alkoxy group, a hydroxy group, a carbonic acid amide group, a sulfonamide group, an urethane bond, a chloromethyl group, a nitro group, an aromatic group containing 6 to 30 carbon atoms and an aromatic heterocyclic group containing 6 to 30 carbon atoms; and  $\text{X}^{\ominus}$  represents an anion; and



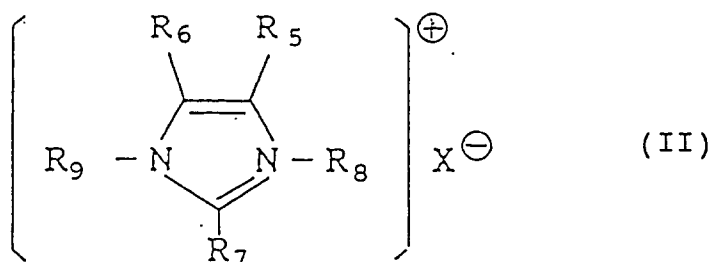
wherein  $\text{R}_{20}$  represents an alkyl group containing 1 to 30 carbon atoms, an aralkyl group containing 7 to 30 carbon atoms or an aryl group containing 6 to 30 carbon atoms which may have one or more members selected from the group consisting of an amino group, an ether bond, a thioether bond, an alkoxy group, a hydroxy group, a carbonic acid amide group, a sulfonamide group, an urethane bond, a chloromethyl group, a nitro group, an aromatic group containing 6 to 30 carbon atoms and an aromatic heterocyclic group containing 6 to 30; and  $\text{X}^{\ominus}$  represents an anion; and wherein said anion is an ion of a halogen atom,  $\text{ClO}_4^-$ ,  $\text{BF}_4^-$ ,  $\text{PF}_4^-$ , sulfate ion, nitrate ion, borate ion, phosphate ion, an organic sulfate ion, an organic phosphate ion, a carbonic acid ion, a tetraphenyl borate ion, a cyanate ion, a phenolate ion, a polyacid ion containing molybdenum or tungsten atom, or an anion of an organic sulfonic acid.

7. An electrophotographic toner obtained by mixing a binder resin, a colorant, and a charge controlling agent composition comprising a quaternary ammonium salt and an inorganic pigment selected from the group consisting of barium sulfate, magnesium hydroxide, aluminum hydroxide, calcium carbonate, magnesium carbonate, barium carbonate, calcium sulfate, zinc silicate, calcium silicate, aluminum silicate, magnesium silicate and magnesium hydrogenphosphate.

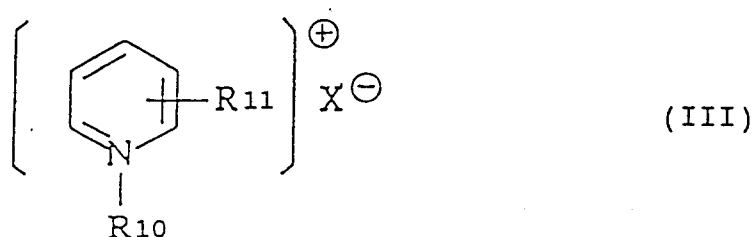
8. The electrophotographic toner of claim 7, wherein said charge controlling agent composition is present in an amount of 0.1 to 15 % by weight in the electrophotographic toner.
9. The electrophotographic toner of claim 7, wherein the weight ratio of said quaternary ammonium salt to said inorganic pigment in said charge controlling agent composition is from 0.5 to 99.5.
10. The electrophotographic toner of claim 7, wherein said charge controlling agent composition is obtained by adding the inorganic pigment or inorganic compounds which forms the inorganic pigment during the preparation of said quaternary ammonium salt, separating the resulting quaternary ammonium salt containing inorganic pigment, then drying the quaternary ammonium salt containing inorganic pigment.
11. The electrophotographic toner of claim 7, wherein said charge controlling agent composition is prepared by mixing the quaternary ammonium salt and the inorganic pigment in the presence of a solvent, and then drying the resulting mixture.
12. The electrophotographic toner of claim 7, wherein said charge controlling agent composition is prepared by mixing and stirring the quaternary ammonium salt and the inorganic pigment so as to adhere the inorganic pigment onto the particles of the quaternary ammonium salt.
13. The electrophotographic toner of claim 7, wherein said quaternary ammonium salt is selected from the following compounds presented by the following formulas (I) to (VII):



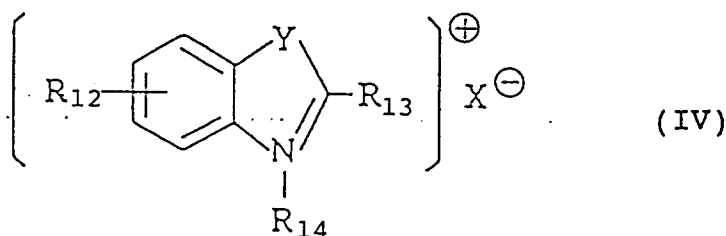
wherein  $R_1$ ,  $R_2$ ,  $R_3$  and  $R_4$  may be the same or different and each represents a hydrogen atom or an alkyl group containing 1 to 30 carbon atoms, an aralkyl group containing 7 to 30 carbon atoms or an aryl group containing 6 to 30 carbon atoms each of which may have one or more members selected from the group consisting of an amino group, an ether bond, a thioether bond, an alkoxy group, a hydroxy group, a carbonic acid amide group, a sulfonamide group, an urethane bond, a chloromethyl group, a nitro group, an aromatic group containing 6 to 30 carbon atoms and an aromatic heterocyclic group containing 6 to 30; and  $X^{\ominus}$  represents an anion;



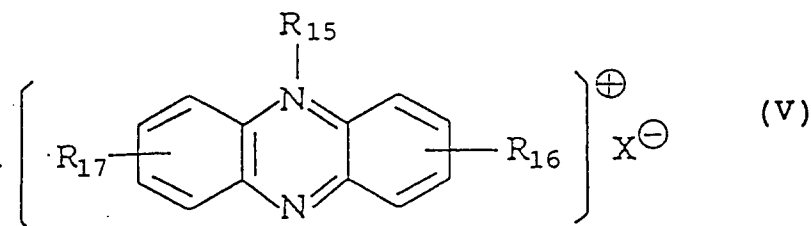
wherein  $R_5$ ,  $R_6$ ,  $R_7$ ,  $R_8$  and  $R_9$  may be the same or different and each represents a hydrogen atom or an alkyl group containing 1 to 30 carbon atoms, an aralkyl group containing 7 to 30 carbon atoms or an aryl group containing 6 to 30 carbon atoms each of which may have one or more members selected from the group consisting of an amino group, an ether bond, a thioether bond, an alkoxy group, a hydroxy group, a carbonic acid amide group, a sulfonamide group, an urethane bond, a chloromethyl group, a nitro group, an aromatic group containing 6 to 30 carbon atoms and an aromatic heterocyclic group containing 6 to 30 carbon atoms; and  $X^{\ominus}$  represents an anion; provided that  $R_5$  and  $R_6$  or  $R_7$  and  $R_8$  may be combined with each other to form an alicyclic or aromatic ring containing 6 to 30 carbon atoms;



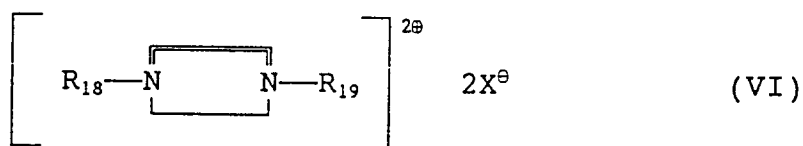
wherein  $\text{R}_{10}$  and  $\text{R}_{11}$  may be the same or different and each represents an alkyl group containing 1 to 30 carbon atoms, an aralkyl group containing 7 to 30 carbon atoms or an aryl group containing 6 to 30 carbon atoms each of which may have one or more members selected from the group consisting of an amino group, an ether bond, a thioether bond, an alkoxy group, a hydroxy group, a carbonic acid amide group, a sulfonamide group, an urethane bond, a chloromethyl group, a nitro group, an aromatic group containing 6 to 30 carbon atoms and an aromatic heterocyclic group containing 6 to 30 carbon atoms; and  $\text{X}^{\ominus}$  represents an anion; provided that  $\text{R}_{11}$  may represent a hydrogen atom;



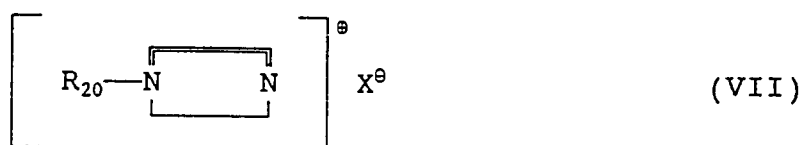
wherein  $\text{R}_{12}$ ,  $\text{R}_{13}$  and  $\text{R}_{14}$  may be the same or different and each represents an alkyl group containing 1 to 30 carbon atoms, an aralkyl group containing 7 to 30 carbon atoms or an aryl group containing 6 to 30 carbon atoms each of which may have one or more members selected from the group consisting of an amino group, an ether bond, a thioether bond, an alkoxy group, a hydroxy group, a carbonic acid amide group, a sulfonamide group, an urethane bond, a chloromethyl group, a nitro group, an aromatic group containing 6 to 30 carbon atoms and an aromatic heterocyclic group containing 6 to 30 carbon atoms; Y presents a carbon, oxygen or sulfur atom; and  $\text{X}^{\ominus}$  represents an anion; provided that  $\text{R}_{13}$  and  $\text{R}_{14}$  may be a hydrogen atom;



wherein  $\text{R}_{15}$ ,  $\text{R}_{16}$  and  $\text{R}_{17}$  may be the same or different and each represents an alkyl group containing 1 to 30 carbon atoms, an aralkyl group containing 7 to 30 carbon atoms or an aryl group containing 6 to 30 carbon atoms each of which may have one or more members selected from the group consisting of an amino group, an ether bond, a thioether bond, an alkoxy group, a hydroxy group, a carbonic acid amide group, a sulfonamide group, an urethane bond, a chloromethyl group, a nitro group, an aromatic group containing 6 to 30 carbon atoms and an aromatic heterocyclic group containing 6 to 30 carbon atoms; and  $\text{X}^{\ominus}$  represents an anion; provided that  $\text{R}_{16}$  and  $\text{R}_{17}$  may represent a hydrogen atom;



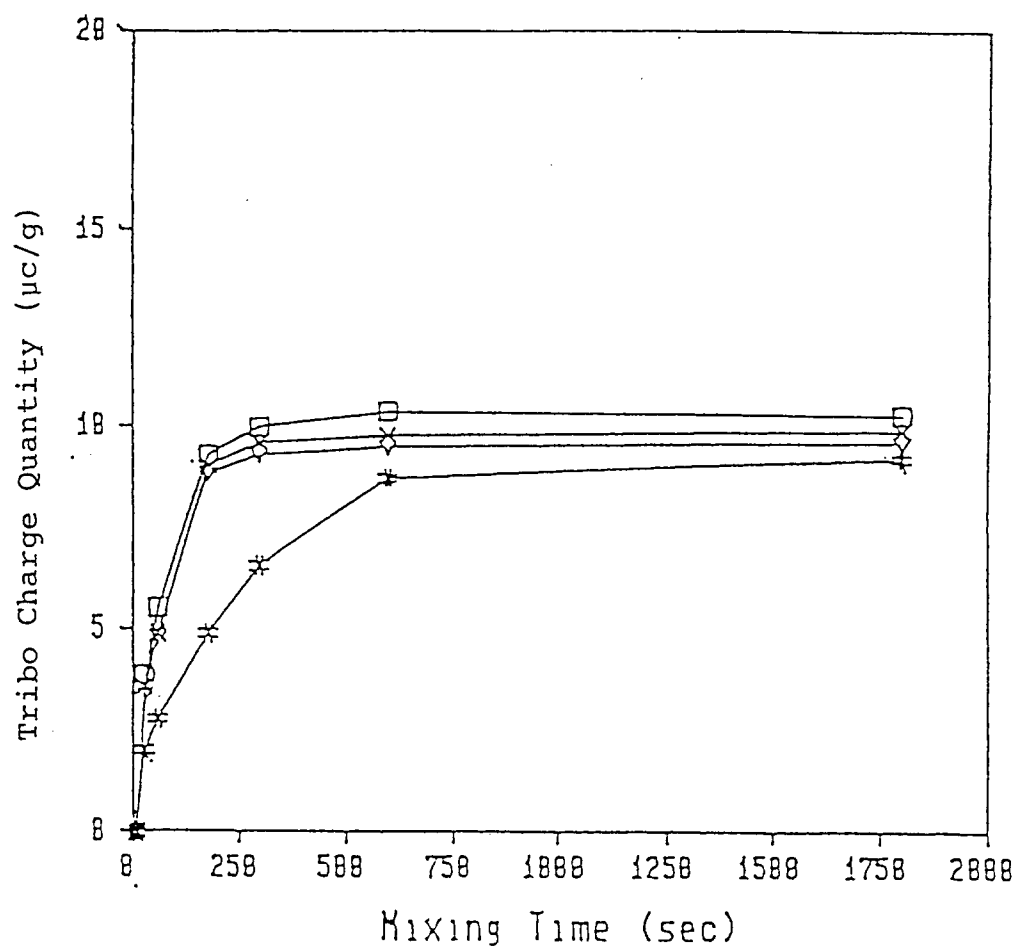
wherein  $\text{R}_{18}$  and  $\text{R}_{19}$  may be the same or different and each represents an alkyl group containing 1 to 30 carbon atoms, an aralkyl group containing 7 to 30 carbon atoms or an aryl group containing 6 to 30 carbon atoms which may have one or more members selected from the group consisting of an amino group, an ether bond, a thioether bond, an alkoxy group, a hydroxy group, a carbonic acid amide group, a sulfonamide group, an urethane bond, a chloromethyl group, a nitro group, an aromatic group containing 6 to 30 carbon atoms and an aromatic heterocyclic group containing 6 to 30 carbon atoms; and  $\text{X}^{\ominus}$  represents an anion; and



wherein  $\text{R}_{20}$  represents an alkyl group containing 1 to 30 carbon atoms, an aralkyl group containing 7 to 30 carbon atoms or an aryl group containing 6 to 30 carbon atoms which may have one or more members selected from the group consisting of an amino group, an ether bond, a thioether bond, an alkoxy group, a hydroxy group, a carbonic acid amide group, a sulfonamide group, an urethane bond, a chloromethyl group, a nitro group, an aromatic group containing 6 to 30 carbon atoms and an aromatic heterocyclic group containing 6 to 30; and  $\text{X}^{\ominus}$  represents an anion; and

wherein said anion is an ion of a halogen atom,  $\text{ClO}_4^-$ ,  $\text{BF}_4^-$ ,  $\text{PF}_4^-$ , sulfate ion, nitrate ion, borate ion, phosphate ion, an organic sulfate ion, an organic phosphate ion, a carbonic acid ion, a tetraphenyl borate ion, a cyanate ion, a phenolate ion, a polyacid ion containing molybdenum or tungsten atom, or an anion of an organic sulfonic acid.



Fig. 1

- Example 1
- ×— Example 2
- ▽— Example 3
- \*— Comparative Example 2



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## EUROPEAN SEARCH REPORT

Application Number

EP 93 10 9119

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
X	US-A-4 828 954 (KEN HASHIMOTO, HIDEAKI AKAGI)	1,4,5,7,8,11,12	G03G9/097
A	* column 6, line 53 - column 7, line 40; claims 1-8,14,15; example 14 *	2,6,9,13	
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X	EP-A-0 347 918 (KONICA CORPORATION)	1,4,5,7,8,11,12	
A	* page 4, line 36 - page 5, line 30 * * page 7, line 49 - page 11, line 48 * * page 13, line 46 - page 14, line 17; claim 1 *	2,6,9,13	
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A	EP-A-0 022 347 (XEROX CORPORATION) * claim 1 *	6,13	
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			TECHNICAL FIELDS SEARCHED (Int. Cl.5)
			G03G
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 13 OCTOBER 1993	Examiner HINDIAS E.
CATEGORY OF CITED DOCUMENTS			
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons ..... & : member of the same patent family, corresponding document	