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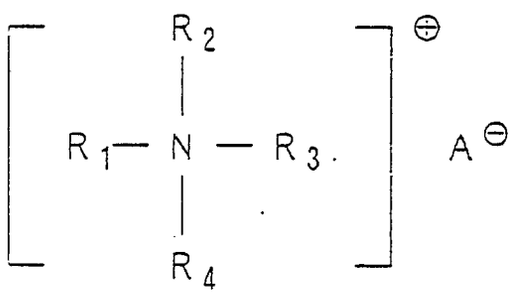
(54) Quaternary ammonium salt and electrophotographic toner.

(57) An electrophotographic toner containing a quaternary ammonium salt having the formula:



(1)

wherein each of R_1 and R_2 is a long chain alkyl group having from 8 to 22 carbon atoms or a long chain

EP 0 284 000 A2

alkenyl group having from 8 to 22 carbon atoms, R_3 is an alkyl group having from 1 to 4 carbon atoms, R_4 is an alkyl group having from 1 to 4 carbon atoms or a benzyl group and $A^{\ominus}$ is an anion.

QUATERNARY AMMONIUM SALT AND ELECTROPHOTOGRAPHIC TONER

The present invention relates to a novel quaternary ammonium salt and an electrophotographic toner.

In electrophotography, it is common that an electrostatic latent image is formed on a photoconductive layer containing a photoconductive material, and the latent image is then developed with a powder developing agent to a visible image, which is then fixed by means of heat or a solvent.

As such a developing agent for electrophotography, a mixture is employed which comprises fine powder called a toner composed of a coloring agent and a resin, and fine glass beads or iron powder called a carrier.

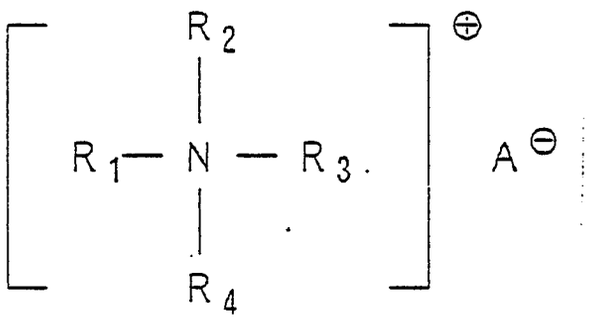
The photoconductive layer can be electrified positively or negatively, so that when it is exposed under an original, an electrostatic image electrified either positively or negatively will be formed. When a negatively electrified electrostatic latent image is developed with a positively electrified toner, a positive image of the original will be obtained.

Usually, a toner is a fine powder of a mixture of a synthetic resin and a coloring agent such as a dyestuff or a pigment. The electrification property of the toner is governed by the resin as the major component thereof. However, it is usually possible to obtain a desired frictional electrification property by an incorporation of a charge-controlling agent.

Conventional charge-controlling agents include pigments and dyestuffs such as oil black, Nigrosine (Japanese Examined Patent Publication No. 25669/1973), aniline black, crystal violet or metal-containing azodyestuffs. Further, as colorless charge-controlling agents, quaternary ammonium salts (Japanese Unexamined Patent Publication No. 119364/1982) and metal soaps are known. However, these charge-controlling agents have disadvantages such that they are likely to be decomposed or modified by humidity, heat, light or mechanical shock, and when they are incorporated in toners, the electrification properties are subject to change due to the change of the environment or during the use for a long period of time, whereby they are likely to give adverse effects to developed images.

Reflecting a recent trend for copying machine for color reproduction, there is an increasing demand for a colorless charge-controlling agent having good properties for the production of a color toner. It is an object of the present invention to overcome the above-mentioned drawbacks and to improve the kick-off speed of frictional electrification which is one of the important properties for a toner.

The present invention provides an electrophotographic toner containing a quaternary ammonium salt having the formula:



(1)

wherein each of R_1 and R_2 is a long chain alkyl group having from 8 to 22 carbon atoms, R_3 is an alkyl group having from 1 to 4 carbon atoms, R_4 is an alkyl group having from 1 to 4 carbon atoms or a benzyl group and $A^{\ominus}$ is an anion.

In the accompanying drawings:

Figure 1 is a graph showing the relation between the stirring time (sec.) and the triboelectric charge (μC/g) with respect to the toners obtained in Example 1 and Comparative Example 1.

Figure 2 is a graph showing the relation between the stirring time and the triboelectric charge with respect to the toners obtained in Example 2 and Comparative Example 2.

Figure 3 is a graph showing the relation between the stirring time and the triboelectric charge with respect to the toners obtained in Example 24 and Comparative Example 3.

Figure 4 is a graph showing the relation between the stirring time and the triboelectric charge with respect to the toners obtained in Example 25 and Comparative Example 4.

Now, the present invention will be described in detail with reference to the preferred embodiments.

The compound of the formula 1 is characterized in that it has two long alkyl groups, whereby the properties of the toner have been substantially improved.

Particularly remarkable as improvement are that by virtue of the two long chain alkyl groups, the compatibility with the binder resin has been improved and that the increasing rate of the triboelectric charge due to the friction of the toner has been increased so that a predetermined level of electric charge can be reached in a short period of time.

The long alkyl group for R_1 and R_2 in the formula 1 includes an octyl group, a decyl group, a dodecyl group, a tetradecyl group, a hexadecyl group, an octadecyl group, an eicosyl group, a docosyl group, an oleyl group, a linolyl group and a hexadecenyl group. Particularly preferred among them is a long chain alkyl group having from 12 to 18 carbon atoms. R_3 includes a methyl group, an ethyl group, a propyl group, a butyl group and a β-hydroxyethyl group. R_4 includes a methyl group, an ethyl group, a propyl group, a butyl group, a β-hydroxyethyl group and a benzyl group. The anion $A^{\ominus}$includes inorganic anions which contain a molybdenum or tungsten atom, such as a molybdic acid ion, a tungstic acid ion, a phosphomolybdic acid ion, a silicomolybdic acid ion, a phosphotungstic acid ion, a silicotungstic acid ion, a phosphotungsten-molybdic acid ion, a silicotungsten-molybdic acid ion and a chromium-molybdic acid ion, and a chlorine ion, a bromine ion, an iodine ion, a nitric acid ion, a sulfuric acid ion, a perchrolic acid ion, a benzoic acid ion, a tetraphenylboron ion, a hexafluorophosphorus ion and a naphtholsulfonic ion.

The compound of the formula 1 is novel when $A^{\ominus}$molybdic acid ion or a tungstic acid ion and provided that when each of R_3 and R_4 is a methyl group, R_1 and R_2 are not simultaneously dodecyl groups or octadecyl groups.

The toner of the present invention contains a binder resin and a coloring agent in addition to the quaternary ammonium salt of the formula 1.

As the binder resin suitable for use for the toner of the present invention, there may be mentioned a homopolymer of styrene or substituted styrene such as a polystyrene or a polyvinyl toluene, a styrene-substituted styrene copolymer, a styrene-acrylate copolymer, a styrene-methacrylate copolymer, a styrene-acrylonitrile copolymer, a polyvinyl chloride, a polyethylene, a silicon resin, a polyester, a polyurethane, a polyamide, an epoxy resin, a modified rosin or a phenol resin.

As the coloring agent, there may be employed, for example, C.I. pigment yellow-12, C.I. solvent yellow 16, 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.

The toner of the present invention may be prepared by melt-mixing the compound of the formula 1 to the synthetic resin in a weight ratio within a range of from 1 to 50%, solidifying the mixture, and then pulverizing it by a ball mill or by other pulverizers. Otherwise, it may be prepared by adding a polymerization initiator to the synthetic resin monomer, then adding the compound of the formula 1 in a weight ratio within a range of from 1 to 50% relative to the monomer, and polymerizing the mixture while suspending it in water. During the preparation, other coloring agents or carbon black may be added as the dyestuff. By the friction with a carrier, the toner thus prepared provides an electric charge suitable for the development of the static latent image, and even when the development is repeated, the electric charge can be maintained at a predetermined level. The charge distribution is uniform, and will be maintained at a constant state.

As the carrier, there may be employed a carrier prepared by coating iron powder or magnetic cores with a styrene-methyl methacrylate copolymer, a silicon resin, a resin mixture of a styrene-methyl methacrylate copolymer and a silicon resin or a tetrafluoroethylene polymer.

Further, the charge controlling agent of the present invention presents excellent electrification properties also when used for a so-called one component toner containing a magnetic powder.

The magnetic material for the magnetic powder may be a fine powder of a metal such as iron, nickel or cobalt, an alloy of a metal such as iron, cobalt, copper, aluminum, nickel or zinc, a metal oxide such as aluminum oxide, iron oxide or titanium oxide, a ferrite of e.g. iron, manganese, nickel, cobalt or zinc, a nitride such as vanadium nitride or chromium nitride, a carbide such as tungsten carbide or silicon carbide or a mixture thereof. The most preferred among them is magnetite.

Now, the present invention will be described with reference to Examples. However it should be understood that the present invention is by no means restricted by these specific Examples. In Examples, "parts" means "parts by weight" unless otherwise specified.

PREPARATION EXAMPLE 1

$(C_{16}H_{33})_2N^{\oplus}(CH_3)_2.1\ 4[Mo_8O_{26}]^{4\ominus}$ (Compound No.1)

10.6 parts of N,N-dimethyl-N,N-dihexadecylammonium chloride was dissolved in 100 parts of methanol. To this solution, an aqueous solution comprising of 9.2 parts of ammonium molybdate tetrahydrate and 60 parts of water were added under stirring. The mixture was stirred at 50°C for 2 hours. The white precipitate was collected by filtration, thoroughly washed with water and dried to obtain 15.0 part of crystals. The crystals were subjected to elemental analysis. The results are shown below.

	Carbon (%)	Hydrogen (%)	Nitrogen (%)
Theoretical value	51.64	9.18	1.77
Measured value	51.43	9.09	1.80

PREPARATION EXAMPLE 2

$(C_{14}H_{29})_2N^{\oplus}(CH_3)_2.1/4[Mo_8O_{26}]^{4\ominus}$ (Compound No.2)

9.5 parts of N,N-dimethyl-N,N-ditetradecylammonium chloride was dissolved in 95 parts of methanol. To this solution, an aqueous solution comprising of 9.2 parts of ammonium molybdate tetrahydrate and 60 parts of water were added under stirring. The mixture was stirred at 50°C for 2 hours. The white precipitate was collected by filtration, thoroughly washed with water and dried to obtain 14.1 parts of crystals. The crystals were subjected to elemental analysis. The results are shown below.

	Carbon (%)	Hydrogen (%)	Nitrogen (%)
Theoretical value	49.04	8.78	1.91
Measured value	48.79	8.73	1.87

PREPARATION EXAMPLE 3

$(C_{14}H_{29})(C_{16}H_{33})N^{\oplus}(CH_3)_2.1/4[Mo_8O_{26}]^{4\ominus}$ (Compound No.6)

10.0 parts of N,N-dimethyl-N-tetradecyl-N-hexadecylammonium chloride was dissolved in 100 parts of methanol. To this solution, an aqueous solution comprising of 9.2 parts of ammonium molybdate tetrahydrate and 60 parts of water were added under stirring. The mixture was stirred at 50°C for 2 hours. The white precipitate was collected by filtration, thoroughly washed with water and dried to obtain 14.3 parts of crystals. The crystals were subjected to elemental analysis. The results are shown below.

	Carbon (%)	Hydrogen (%)	Nitrogen (%)
Theoretical value	50.39	8.99	1.84
Measured value	50.51	8.84	1.80

PREPARATION EXAMPLE 4

$(C_{18}H_{37})_2N^{\oplus}(C_4H_9)_2.1/4[Mo_8O_{26}]^{4\ominus}$ (Compound No.7)

13.4 parts of N,N-dibutyl-N,N-dioctadecylammonium chloride was dissolved in 130 parts of methanol. To this solution, an aqueous solution comprising of 9.2 parts of ammonium molybdate tetrahydrate and 60 parts of water were added under stirring. The mixture was stirred at 50°C for 2 hours. The white precipitate was collected by filtration, thoroughly washed with water and dried to obtain 17.5 parts of crystals. The crystals were subjected to elemental analysis. The results are shown below.

	Carbon (%)	Hydrogen (%)	Nitrogen (%)
Theoretical value	56.76	9.96	1.50
Measured value	56.84	9.79	1.48

PREPARATION EXAMPLE 5

$(C_{18}H_{35})_2N^{\oplus}(CH_3)_2.1/4[Mo_8O_{26}]^{4\ominus}$ (Compound No. 10)

11.6 g of N,N-dimethyl-N,N-dioleylammonium chloride was dissolved in 110 parts of methanol. To this solution, an aqueous solution comprising of 9.2 parts of ammonium molybdate tetrahydrate and 60 parts of water were added under stirring. The mixture was stirred at 50°C for 2 hours. The white precipitate was collected by filtration, thoroughly washed with water and dried to obtain 15.6 parts of crystals. The crystals were subjected to elemental analysis. The results are shown below.

	Carbon (%)	Hydrogen (%)	Nitrogen (%)
Theoretical value	54.15	9.09	1.66
Measured value	54.01	9.01	1.70

PREPARATION EXAMPLE 6

$(C_{18}H_{37})_2N^{\oplus}(CH_3)_2.1\ 10[H_2W_{12}O_{42}]^{10\ominus}$ (Compound No. 14)

11.7 parts of N,N-dimethyl-N,N-dioctodecylammonium chloride was dissolved in 110 parts of methanol. To this solution, an aqueous solution comprising of 8.4 g of ammonium paratungstate hexahydrate and 50 parts of water were added under stirring. The mixture was stirred at 50°C for 2 hours. The white precipitate was collected by filtration, thoroughly washed with water and dried to obtain 15.4 parts of crystals. The crystals were subjected to elemental analysis. The results are shown below.

	Carbon (%)	Hydrogen (%)	Nitrogen (%)
Theoretical value	54.39	9.64	1.67
Measured value	54.21	9.69	1.65

PREPARATION EXAMPLES 7 to 23

The following compounds were prepared in the same manner as in the preceding Preparation Examples.

PREPARATION EXAMPLE 7: $(C_{18}H_{37})(C_{12}H_{25})N^{\oplus}(CH_3)_2.1/4[Mo_8O_{26}]^{4\ominus}$ (Compound No. 3)

PREPARATION EXAMPLE 8: $(C_{18}H_{37})(C_{14}H_{25})N^{\oplus}(CH_3)_2.1/4[Mo_8O_{26}]^{4\ominus}$ (Compound No. 4)

PREPARATION EXAMPLE 9: $(C_{18}H_{37})(C_{16}H_{33})N^{\oplus}(CH_3)_2.1/4[Mo_8O_{26}]^{4\ominus}$ (Compound No. 5)

PREPARATION EXAMPLE 10: $(C_{16}H_{33})_2N^{\oplus}(C_4H_9)_2.1/4[Mo_8O_{26}]^{4\ominus}$ (Compound No. 8)

PREPARATION EXAMPLE 11: $(C_{14}H_{29})_2N^{\oplus}(C_4H_9)_2.1/4[Mo_8O_{26}]^{4\ominus}$ (Compound No. 9)

PREPARATION EXAMPLE 12: $(C_{18}H_{33})_2N^{\oplus}(CH_3)_2.1/4[Mo_8O_{26}]^{4\ominus}$ (Compound No. 11)

PREPARATION EXAMPLE 13: $(C_{16}H_{31})_2N^{\oplus}(CH_3)_2.1/4[Mo_8O_{26}]^{4\ominus}$ (Compound No. 12)

PREPARATION EXAMPLE 14: $(C_{18}H_{37})(C_{18}H_{35})N^{\oplus}(CH_3)_2.1/4[Mo_8O_{26}]^{4\ominus}$ (Compound No. 13)

PREPARATION EXAMPLE 15: $(C_{16}H_{33})_2N^{\oplus}(CH_3)_2.1\ 10[H_2W_{12}O_{42}]^{10\ominus}$
(Compound No. 15)

PREPARATION EXAMPLE 16: $(C_{14}H_{29})_2N^{\oplus}(CH_3)_2.1.10[H_2W_{12}O_{42}]^{10\ominus}$
(Compound No. 16)

PREPARATION EXAMPLE 17: $(C_{16}H_{33})(C_{14}H_{29})N^{\oplus}(CH_3)_2.1/10[H_2W_{12}O_{42}]^{10\ominus}$
(Compound No. 17)

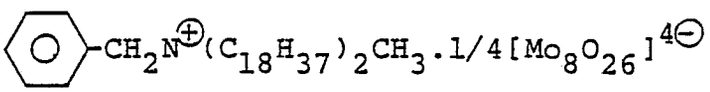
PREPARATION EXAMPLE 18: $(C_{12}H_{25})_2N^{\oplus}(C_4H_9)_2.1/10[H_2W_{12}O_{42}]^{10\ominus}$
(Compound No. 18)

PREPARATION EXAMPLE 19: $(C_{18}H_{35})_2N^{\oplus}(CH_3)_2.1.10[H_2W_{12}O_{42}]^{10\ominus}$
(Compound No. 19)

PREPARATION EXAMPLE 20: $(C_{18}H_{37})(C_{18}H_{35})N^{\oplus}(CH_3)_2.1/10[H_2W_{12}O_{42}]^{10\ominus}$
(Compound No. 20)

PREPARATION EXAMPLE 21: $(C_{18}H_{33})_2N^{\oplus}(CH_3)_2.1/10[H_2W_{12}O_{42}]^{10\ominus}$
(Compound No. 21)

PREPARATION EXAMPLE 22:



(Compound No. 22)

PREPARATION EXAMPLE 23: $(C_{12}H_{25})_2N^{\oplus}(CH_2CH_2OH)_2.1/4[Mo_8O_{26}]^{4\ominus}$
(Compound No. 23)

EXAMPLE 1

One part of $(C_{16}H_{33})_2N^{\oplus}(CH_3)_2.1/4[Mo_8O_{26}]^{4\ominus}$ (Compound No. 1) and 5 parts of carbon black were kneaded with 100 parts of a styrene-n-butyl methacrylate copolymer under heating. After cooling, the mixture was pulverized by a hammer mill, then finely pulverized by a jet pulverizer and classified to obtain a powder having a particle size of from 10 to 12 μm. The black powder thus obtained was mixed with an iron powder carrier in a weight ratio of 5 : 150, and the mixture was shaked. The toner was positively electrified, and the electric charge was 35 μC/g. By using this toner, an image was reproduced by a commercially available photocopying machine, whereby copies with a sharp image quality were obtained from the initial stage and high quality images with no substantial change were obtained even after the reproduction of 10,000 copies.

COMPARATIVE EXAMPLE 1

A toner was prepared in the same manner as in Example 1 except that instead of the quaternary ammonium salt used in Example 1, N,N,N-trimethyl-N-hexadecylammonium molybdate was used. Namely, the quaternary ammonium salt used in this Comparative Example is different from the one used in Example 1 in that one of the two long chain alkyl groups (hexadecyl groups) of the quaternary ammonium salt used in Example 1 was substituted by a lower alkyl group (methyl group). The toners of Example 1 and Comparative Example 1 were put in polypropylene containers, respectively, and stirred at a speed of about 100 rpm, and the triboelectric charges of the toners were measured as time passed. The results are shown in Figure 1. From this Figure, it is apparent that in Example 1, the increase of the electric charge is quick from the initial stage of stirring, whereas in Comparative Example 1, the increase of electric charge is slow at the initial stage of stirring. Also in this respect, the toner of the present invention i.e. the toner containing a quaternary ammonium salt having two long chain alkyl groups, is superior.

EXAMPLE 2

1.5 parts of $(C_{14}H_{29})_2N^{\oplus}(CH_3)_2.1/4[Mo_8O_{25}]^{4\ominus}$(Compound No. 2) and 5 parts of carbon black were kneaded with 100 parts of a styrene-n-butyl methacrylate copolymer under heating, followed by the same treatment as in Example 1 to obtain a black toner. This toner was positively charged, and the electric charge was 32 $\mu C/g$. By using this toner, an image was reproduced by a commercially available photocopying machine, whereby copies with an excellent image quality were obtained not only at the initial stage but also after the reproduction of 10,000 copies.

COMPARATIVE EXAMPLE 2

A toner was prepared in the same manner as in Example 2 except that instead of the quaternary ammonium salt used in Example 2, N,N,N-trimethyl-N-tetradecylammonium molybdate was used. Namely, the quaternary ammonium salt used in this Comparative Example is different from the one used in Example 2 in that one of the two long chain alkyl groups (tetradecyl groups) of the quaternary ammonium salt used in Example 2 was substituted by a lower alkyl group (methyl group). The toners of Example 2 and this Comparative Example were put in propylene containers, respectively, and stirred at a speed of about 100 rpm, and the triboelectric charges of the toners were measured as the time passed. The results are shown in Figure 2. From this Figure, it is apparent that in Example 2, the increase of electric charge is quick from the initial stage of stirring, whereas in Comparative Example 2, the increase of electric charge is slow at the initial stage of stirring. Also in this respect, the toner of the present invention i.e. the toner containing a quaternary ammonium salt having two long chain alkyl groups, is superior.

EXAMPLES 3 to 23

Toners were prepared in the same manner as in Example 1 except that the quaternary ammonium salt was changed. The results are shown in Table 1.

Table 1

Example No.	Compound No. of the quaternary ammonium salt used	Electric charge of toner (μc/g)
3	3	30
4	4	30
5	5	36
6	6	34
7	7	35
8	8	29
9	9	32
10	10	28
11	11	34
12	12	31
13	13	34
14	14	35
15	15	28
16	16	31
17	17	29
18	18	33
19	19	28
20	20	32
21	21	30
22	22	33
23	23	27

EXAMPLE 24

One part of N,N-dimethyl-N,N-dioctadecylammonium chrolide and 5 parts of carbon black were kneaded with 100 parts of a styrene-n-butyl methacrylate copolymer under heating. After cooling, the mixture was pulverized by a hammer mill, then finely pulverized by a jet pulverizer and classified to obtain a powder having a particle size of from 10 to 12 μm. The black powder thus obtained was mixed with an iron powder carrier in a weight ratio of 5 : 150, and the mixture was shaked. The toner was positively electrified, and the electric charge was 22 μC/g. By using this toner, an image was reproduced by a commercially available photocopying machine, whereby copies with a sharp image quality were obtained from the initial stage and high quality images with no substantial change were obtained even after the reproduction of 10,000 copies.

COMPARATIVE EXAMPLE 3

A toner was prepared in the same manner as in Example 24 except that instead of the quaternary ammonium salt used in Example 24, N,N,N-trimethyl-N-octadecylammonium chloride was used. Namely, the quaternary ammonium salt used in this Comparative Example is different from the one used in Example 24 in that one of the two long chain alkyl groups (octadecyl groups) of the quaternary ammonium salt used in Example 24 was substituted by a lower alkyl group (methyl group). The toners of Example 24 and Comparative Example 3 were put in polypropylene containers, respectively, and stirred at a speed of about 100 rpm, and the triboelectric charges of the toners were measured as time passed. The results are shown in Figure 3. From this Figure, it is apparent that in Example 24, the increase of the electric charge is quick from the initial stage of stirring, whereas in Comparative Example 3, the increase of electric charge is slow at the initial stage of stirring. Also in this respect, the toner of the present invention i.e. the toner containing a quaternary ammonium salt having two long chain alkyl groups, is superior.

EXAMPLE 25

1.5 parts of N,N-dimethyl-N,N-dioctadecylammonium molybdate (which can be obtained in the form of precipitates by adding an aqueous ammonium molybdate to a solution of N,N-dimethyl-N,N-dioctadecylammonium chloride in a mixture of an alcohol and water) and 5 parts of carbon black were kneaded with 100 parts of a styrene-n-butyl methacrylate copolymer under heating, followed by the same treatment as in Example 24 to obtain a black toner. This toner was positively charged, and the electric charge was 35 μC/g. By using this toner, an image was reproduced by a commercially available photocopying machine, whereby copies with an excellent image quality were obtained not only at the initial stage but also after the reproduction of 10,000 copies.

COMPARATIVE EXAMPLE 4

A toner was prepared in the same manner as in Example 25 except that instead of the quaternary ammonium salt used in Example 25, N,N,N-trimethyl-N-octadecylammonium molybdate was used. Namely, the quaternary ammonium salt used in this Comparative Example is different from the one used in Example 25 in that one of the two long chain alkyl groups (octadecyl groups) of the quaternary ammonium salt used in Example 25 was substituted by a lower alkyl group (methyl group). The toners of Example 25 and this Comparative Example were put in propylene containers, respectively, and stirred at a speed of about 100 rpm, and the triboelectric charges of the toners were measured as the time passed. The results are shown in Figure 4. From this Figure, it is apparent that in Example 25, the increase of electric charge is quick from the initial stage of stirring, whereas in Comparative Example 4, the increase of electric charge is slow at the initial stage of stirring. Also in this respect, the toner of the present invention i.e. the toner containing a quaternary ammonium salt having two long chain alkyl groups, is superior.

EXAMPLE 26

A toner was prepared in the same manner as in Example 24 except that instead of N,N-dimethyl-N,N-dioctadecylammonium chloride, N,N-dimethyl-N,N-di-hardened beef tallow alkyl ammonium molybdate [which can be prepared by adding an aqueous ammonium molybdate solution to a solution of N,N-dimethyl-N,N-di-hardened beef tallow alkyl ammonium chloride (Nissan cation 2-ABT, manufactured by Nippon Yushi K.K.; the long chain alkyl moiety is a mixture of $C_{18}/C_{16}/C_{14}$ = 66/30/4) in a mixture of an alcohol and water] was used. This toner was positively charged, and the charge was 33 μC/g. By using this toner, an image was reproduced by a commercially available photocopying machine, whereby copies with an excellent image quality were obtained not only at the initial stage but also after the reproduction of 10,000 copies.

EXAMPLES 27 to 47

Toners were prepared in the same manner as in Example 24 except that the quaternary ammonium salt was changed. The results are shown in Table 2.

Table 2

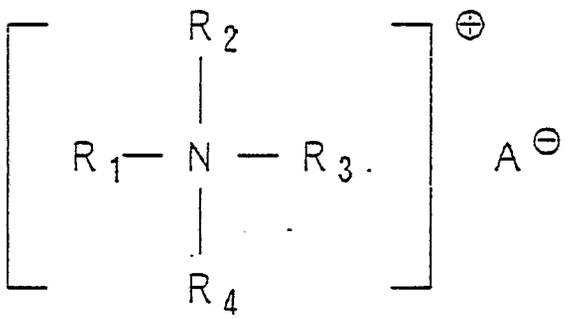
Example No.	Quaternary ammonium salts		Electric charge of toner (μC/g)
	Ammonium moiety	Counter ion	
27	N,N-dimethyl-N,N-dioctadecylammonium	Phosphotungstic acid ion	30
28	"	Tetraphenylboron ion	18
29	"	Hexafluorophosphorus ion	20
30	"	Tetrafluoroboron ion	27
31	"	1-naphthol-4-sulfonic acid ion	34
32	"	Chromium-molybdic acid ion	32
33	"	P-toluene sulfonic acid ion	28
34	"	Phosphomolybdic acid ion	33
35	"	Perchloric acid ion	25
36	"	Bromine ion	27
37	N-methyl-N-benzyl-N,N-dioctadecyl-ammonium	Molybdic acid ion	33
38	N,N-dimethyl-N,N-dihexadecylammonium	"	35
39	N,N-dimethyl-N,N-ditetradecylammonium	"	32
40	N,N-dimethyl-N,N-didodecylammonium	"	29
41	N,N-dimethyl-N-dodecyl-N-octadecyl-ammonium	"	30
42	N,N-dimethyl-N-tetradecyl-N-octadecyl-ammonium	"	30

Table 2 (continued)

Example No.	Quaternary ammonium salts		Electric charge of toner (μC/g)
	Ammonium moiety	Counter ion	
43	N,N-dimethyl-N-hexadecyl-N-octadecylammonium	Molybdic acid ion	36
44	N,N-dibutyl-N,N-dioctadecylammonium	"	35
45	N,N-dimethyl-N,N-dioleylammonium	"	28
46	N,N-dimethyl-N,N-dilinolylammonium	"	34
47	N,N-di-β-hydroxyethyl-N,N-didodecyl-ammonium	"	27

Claims

1. A quaternary ammonium salt having the formula:



(1)

wherein each of R_1 and R_2 is a long chain alkyl group having from 8 to 22 carbon atoms or a long chain alkenyl group having from 8 to 22 carbon atoms, R_3 is an alkyl group having from 1 to 4 carbon atoms, R_4 is an alkyl group having from 1 to 4 carbon atoms or a benzyl group and $A^{\ominus}$ is a molybdic acid ion or a tungstic acid ion, provided that when each of R_3 and R_4 is a methyl group, R_1 and R_2 are not simultaneously dodecyl groups or octadecyl groups.

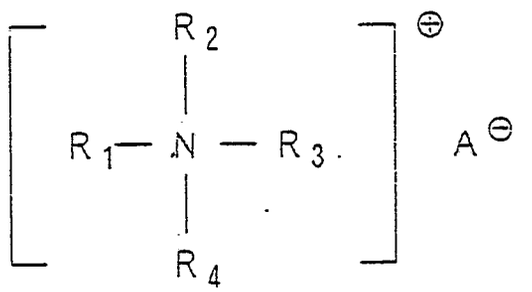
2. The quaternary ammonium salt according to Claim 1, which is $(C_{16}H_{33})_2N^{\oplus}(CH_3)_2.1/4[Mo_8O_{26}]^{4\ominus}$.

3. The quaternary ammonium salt according to Claim 1, which is $(C_{16}H_{33})_2N^{\oplus}(CH_3)_2.1/6[Mo_7O_{24}]^{6\ominus}$.

4. The quaternary ammonium salt according to Claim 1, which is $(C_{14}H_{29})_2N^{\oplus}(CH_3)_2.1/4[Mo_8O_{26}]^{4\ominus}$.

5. The quaternary ammonium salt according to Claim 1, which is $(C_{14}H_{29})_2N^{\oplus}(CH_3)_2.1/6[Mo_7O_{24}]^{6\ominus}$.

6. An electrophotographic toner containing a quaternary ammonium salt having the formula:



(1)

wherein each of R_1 and R_2 is a long chain alkyl group having from 8 to 22 carbon atoms or a long chain alkenyl group having from 8 to 22 carbon atoms, R_3 is an alkyl group having from 1 to 4 carbon atoms, R_4 is an alkyl group having from 1 to 4 carbon atoms or a benzyl group and $A^{\ominus}$ is an anion.

7. The electrophotographic toner according to Claim 6, wherein the anion is selected from the group consisting of a molybdic acid ion, a tungstic acid ion, a phosphomolybdic acid ion, a silicomolybdic acid ion, a phosphotungstic acid ion, a silicotungstic acid ion, a phosphotungsten-molybdic acid ion, a silicotungsten-molybdic acid ion, a chromium-molybdic acid ion, a chlorine ion, a bromine ion, an iodine ion, a nitric acid ion, a sulfuric acid ion, a perchloric acid ion, a benzoic acid ion, a tetraphenylboron ion, a hexafluorophosphorus ion and a naphtholsulfonic acid ion.

8. The electrophotographic toner according to Claim 7, wherein each of R_1 and R_2 is an octyl group, a decyl group, a dodecyl group, a tetradecyl group, a hexadecyl group, an octadecyl group, an eicosyl group, a docosyl group, an oleyl group, a linolyl group or a hexadecenyl group, and R_3 is a methyl group, an ethyl group, a propyl group, a butyl group, or a β-hydroxyethyl group, and R_4 is a methyl group, an ethyl group, a propyl group, a butyl group, a β-hydroxyethyl group or a benzyl group.

9. The electrophotographic toner according to Claim 7, wherein each of R_1 and R_2 is a long chain alkyl group having from 12 to 18 carbon atoms.

FIGURE 1

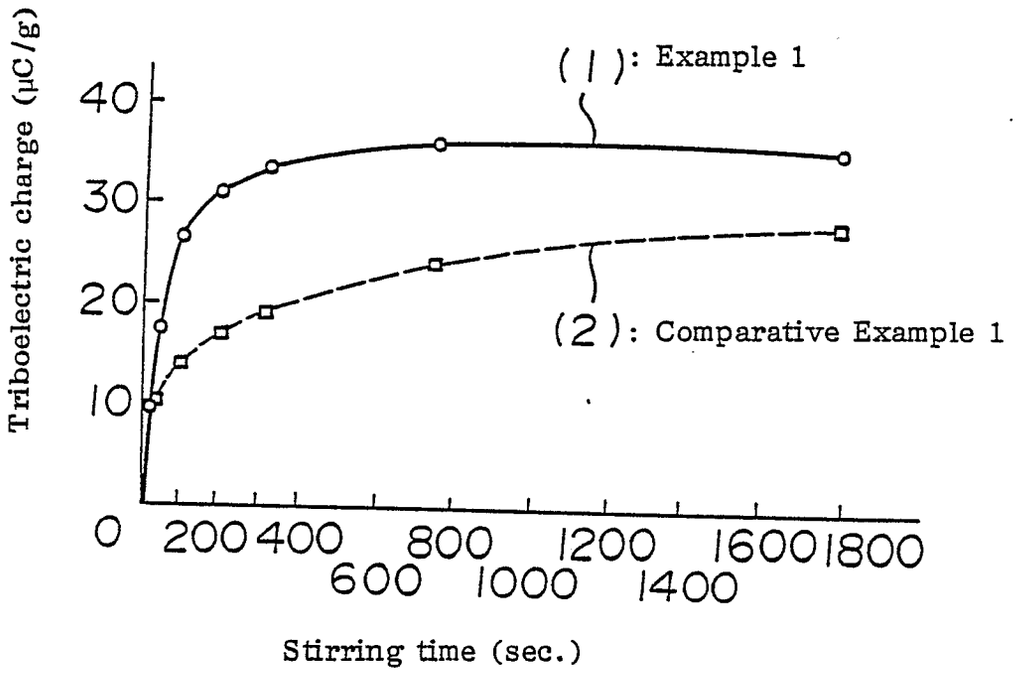


FIGURE 2

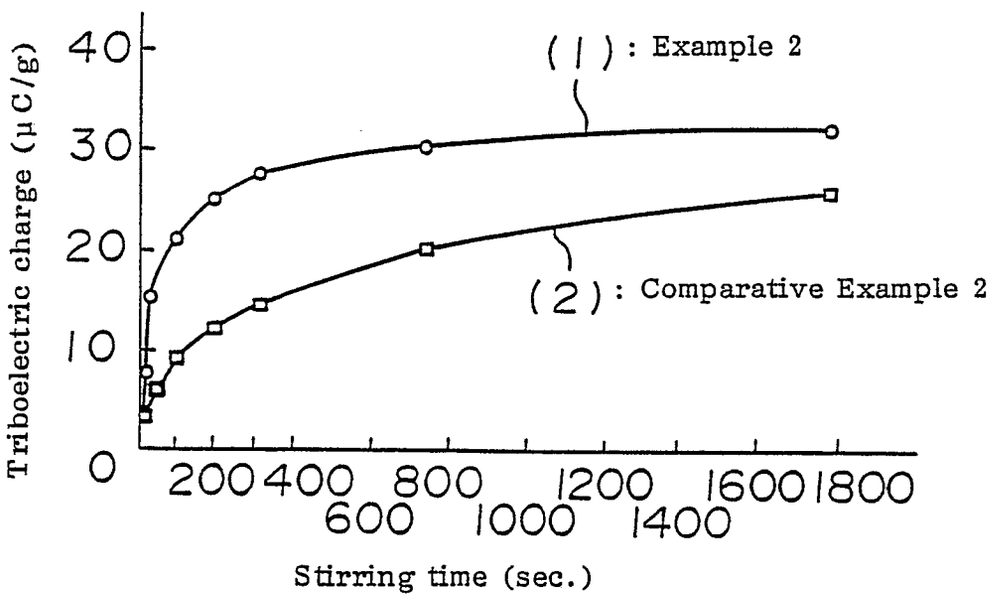


FIGURE 3

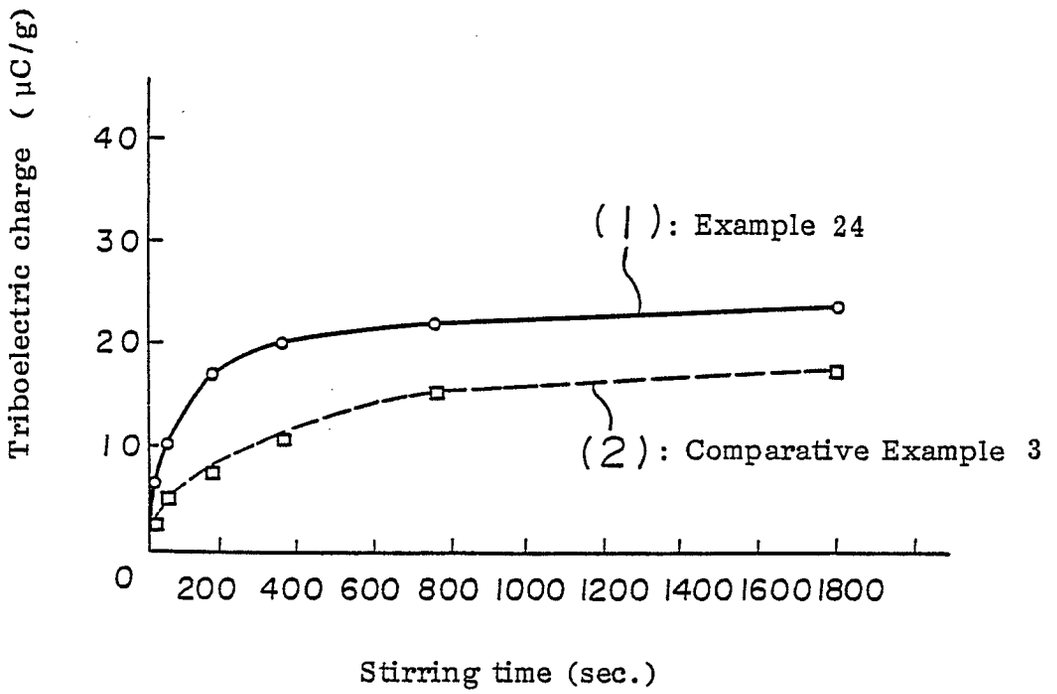


FIGURE 4