

The present invention relates to the use of highly fluorinated ammonium and immonium compounds as colorless charge regulation agents for use in toners and developers for electrophotographic copying processes. As a result of
5 the selective introduction of fluorine-containing organic radicals, the compounds according to the invention have particularly beneficial charge regulation properties.

In electrophotographic copying processes, a "latent charge image" is produced on a photoconductor. This is
10 done, for example, by charging up a photoconductor by means of a corona discharge and then exposing the electrostatically charged-up surface of the photoconductor to an image, in which process the exposure brings about the charge drainage to the earthed substrate at the exposed
15 points. The "latent charge image" produced in this way is then developed by applying a toner. In a subsequent step, the toner is transferred from the photoconductor to, for example, paper, textiles, films or plastic and fixed thereon, for example, by pressure, radiation, heat or
20 exposure to solvent. The photoconductor used is then cleaned and is available for a new copying process.

Numerous patents describe the optimization of toners, in which connection, inter alia, the effect of the toner binder (variation of resin/resin components or wax/wax
25 components), the effect of regulation agents or other additives or the effect of carriers (in the case of two-component developers) and magnetic pigments (in the case of single-component developers) were investigated (US-PS 2,221,776).

30 A measure of the quality of a toner is its specific chargeability Q/M (charge per unit mass). In addition to the sign and magnitude of the electrostatic charging, the rapid achievement of the desired magnitude of charging and the constancy of this charge throughout a prolonged
35 activation period are, in particular, a decisive quality criterion. In practice, this is of central importance inasmuch as the toner may be exposed to a considerable

activation time in the developer mixture before it is transferred to the photoconductor, since it sometimes remains in the developer mixture for a period in which up to several thousand copies are produced. In addition, the
5 insensitivity of the toner to climatic effects such as temperature and atmospheric humidity is a further important criterion of suitability.

Both positively and negatively chargeable toners are used in copiers and laser printers, depending on the type of
10 process and type of equipment.

In order to obtain electrophotographic toners or developers having either positive or negative triboelectric chargeability, so-called charge regulation agents (also called charge regulation agents) are often added. In this
15 connection, in addition to the sign of the charge regulation, the extent of the regulating effect is of importance since a higher effectiveness makes it possible to use a smaller amount.

Since, as a rule, toner binders alone produce a
20 considerable change in the charging depending on the activation time, the object of a charge regulation agent is, on the one hand, to establish the sign and magnitude of the toner charging and, on the other, to counteract the charging drift of the toner binder and to ensure constancy of the toner charging. Charge regulation agents
25 which are incapable of preventing the toner or developer exhibiting a high charging drift (aging) during a prolonged period of use and which may even result in the toner or developer undergoing a charge reversal are
30 therefore unsuitable for practical use.

Full-color copiers and full-color laser printers employ the principle of trichromatism which makes an exact hue matching of the three primary colors (yellow pigment, cyan pigment and magenta pigment) necessary. The slight-
35 est displacements in the hue of even only one of the

three primary colors requires of necessity a displacement in the hue of the two other colors in order to be able to produce full-color copies or full-color prints true to the original even under those circumstances. Owing to the
5 precise matching of the coloristics of the individual pigments to one another, necessary in color toners, charge regulation agents having absolutely no inherent color are very particularly important.

In color toners, the three toners yellow, cyan and
10 magenta have to be precisely matched to one another not only in relation to the precisely defined color requirements, but also in relation to their triboelectric properties. This triboelectric matching is necessary because, in the case of a full-color print or in the case
15 of a full-color copy, the three color toners (or four color toners if black is included) have to be transferred consecutively in the same equipment.

It is known that color pigments may sometimes have a very intense effect on the triboelectric charging of toners
20 (H.-T. Macholdt, and A. Sieber, Dyes & Pigments 9 (1988), 119-27; US-PS 4,057,426; EP-A-247,576). Owing to the different triboelectric effects of color pigments and the very marked effects on the toner chargeability sometimes resulting therefrom, it is not possible to add them as
25 the sole colorant to a toner base formulation once it has been produced. On the contrary, it may be necessary to produce for each colorant a particular formulation for which, for example, the type and amount of the charge regulation agent needed are specifically designed. This
30 procedure is correspondingly elaborate and, in the case of color toners for process color (trichromatism), adds still further to the difficulties already described. Highly effective, colorless charge regulation agents which are capable of compensating for the differing
35 triboelectric behavior of different pigments and imparting the required charging to the toner are therefore required. In this manner, triboelectrically very

different pigments can be used in the different toners necessary (yellow, cyan, magenta) on the basis of a toner base formulation containing one and the same charge regulation agent once the formulation has been produced.

5 Colorless charge regulation agents for electrophotographic toners and developers which have been described are ammonium compounds (for example, EP-A-203,532, EP-A-242,420, US-PS 4,683,188, US-PS 4,684,596) and phosphonium compounds (for example, US-PS 3,893,935, US-PS
10 4,496,643), metal complexes and organometallic compounds (for example, US-PS 4,656,112, DE-A-3,144,017, JP-A-61-236,557, JP-A-62-127,754, JP-A-62-287,262), and also a number of other compounds (for example, EP-A-216,295).

Positive colorless charge regulation agents essentially
15 include quaternary ammonium compounds and phosphonium compounds and also some organotin and organoantimony compounds. However, the colorless charge regulation agents known hitherto have a number of disadvantages which severely limit their use in practice or in some
20 cases even make it impossible. Thus, the quaternary ammonium compounds, which are suitable per se, are difficult to disperse and may result in non-uniform charging of the toner, and the toner charge they produce is not stable over a prolonged activation time, in
25 particular at high temperature and atmospheric humidity (EP-A-242,420). Furthermore, such compounds may be sensitive to light or mechanical effects (EP-A-203,532, US-PS 4,683,188) and thermally labile, and may yield decomposition products which may be disadvantageous for
30 the triboelectric charging of the toner (US-PS 4,684,596). In addition, they often exhibit wax-like behavior, and in some cases solubility in water and low effectiveness as charge regulation agents (see Comparison Examples).

35 Phosphonium salts are less effective than ammonium salts as charge regulation agents (US-PS 4,496,643) and may

present toxicological problems. Thus, for example, tetra-n-butylphosphonium bromide (US-PS 3,893,935), which is known as a charge regulation agent, is a strong skin and mucous membrane irritant.

- 5 Organotin borates as described in EP-A-216,295, and also organotin compounds (JP-A-62-287,262) and organoantimony compounds (JP-A-61-236,557) present problems owing to their heavy-metal content.

10 The known negative colorless charge regulation agents are almost exclusively heavy-metal compounds, namely chromium complexes, iron complexes, cobalt complexes (DE-A-3,144,017) and zinc complexes (US-PS 4,656,112, JP-A-62-127,754). In addition to the heavy-metal problems, it is also a disadvantage that some of these compounds are not
15 really colorless and consequently find only limited use in color toners.

In addition to incorporation in the toner resin, charge regulation agents are also used for coating carriers. In this case, the same compound classes are used as for
20 incorporation in toner resins, for example ammonium compounds (JP-A-61-258,270) and phosphonium compounds (JP-A-61-260,258), and also heavy-metal complexes and heavy-metal organic compounds (JP-A-61-147,261, JP-A-61-259,267).

25 DE-A-29 40 907 describes a magnetic toner which is composed of a magnetic material, a binding resin and a fluorine-containing compound which coats the surface of the magnetic material completely. A homogenous incorporation of said fluorine-containing compound into the
30 binding resin is not, however, carried out, but is felt, in contrast, to be extremely disadvantageous.

Basically, it may be stated that colorless charge regulation agents are in principle known both for positive toners and for negative toners, but are only of limited

suitability for use in practice, or are unusable, or still require substantial improvement.

The object of the present invention was therefore to find improved charge regulation agents which are distinguished
5 by the absolute absence of an inherent color, have a higher effectiveness, are suitable, in particular, for use in color toners, and adjust the electrostatic charging of toners and developers rapidly and as a function of concentration. Furthermore, they should keep
10 the electrostatic charging constant over a prolonged activation period (no aging), function satisfactorily, especially at high atmospheric humidity, and be compatible with common toner resins and readily dispersible.

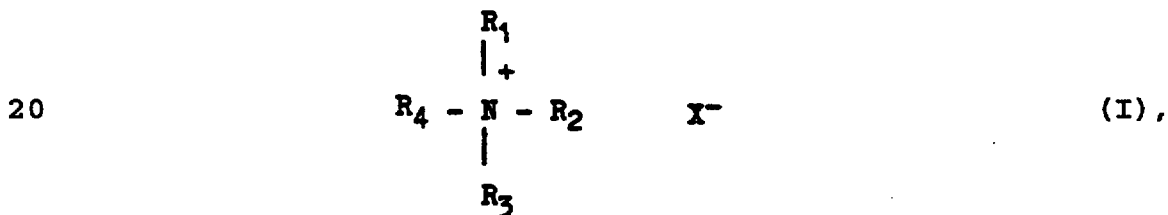
15 Surprisingly, it has now emerged that ammonium compounds and immonium compounds which are as highly fluorinated as possible have particularly beneficial properties as colorless charge regulation agents for electrophotographic toners and developers. Because of their color-
20 lessness, high effectiveness, good compatibility and dispersibility in common toner resins and chemical inertness, the compounds are suitable, in particular, for use in color toners or color developers for full-color copiers based on the principle of trichromatism (sub-
25 tractive color mixing), and even for colored toners or developers in general and for black toners or developers. Particularly surprising is the fact that substances one and the same compound class, depending on the chemical modification, are suitable either as positive or as
30 negative charge regulation agents (see Application Examples 2 and 4). Furthermore, the compounds are also suitable for coating carriers.

A considerable technical advantage of these readily dispersible compounds is that substances of the same
35 compound class can be used either as positive or as negative regulation agents. Consequently, problems with

incorporation into the toner binder and compatibility with the toner binder after producing a toner base formulation are minimized. Thus, positive toners and also negative toners can be produced on the basis of a fixed
 5 toner base formulation (composed of toner binder, pigment, flow promoter and other constituents) by incorporating the desired regulation agent.

The synthesis of fluorinated quaternary ammonium compounds and immonium compounds is known and is described
 10 in US-PS 3,535,381, FR-PS 2,153,489, DE-A-1,922,277, DE-A-2,244,297 and also DE-A-3,306,933. Such compounds are used, for example, as surface-active substances, emulsifiers and flow accelerators as described in DE-A-2,244,297, DE-PS 2,749,330, DE-A-3,347,378 and BE-PS
 15 788,335. Completely novel, however, is their use as charge regulation agents in electrophotographic toners and developers.

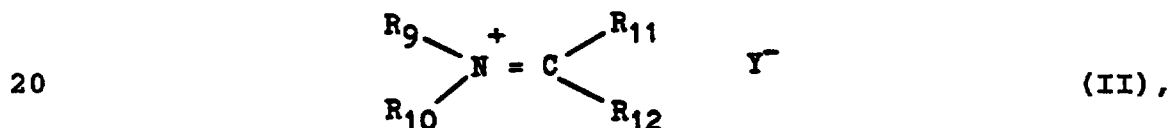
The present invention relates to the use of highly fluorinated ammonium compounds of the formula (I)



in which R_1 to R_4 denote hydrogen atoms or organic radicals, at least one of the radicals R_1 to R_4 denoting a straight-chain or branched fluorine-containing alkyl radical or fluorine-containing alkenyl radical which
 25 contains 1 to 69 carbon atoms and 3 to 66 fluorine atoms and which may contain hydroxyl and/or chloromethyl and/or carboxamide and/or sulfonamide and/or urethane and/or amino and/or R_5-O-R_6 and/or $R_7-\overset{\overset{O}{\parallel}}{C}-O-R_8$ groups in which

30 R_5 , R_6 , R_7 and R_8 are (C_1-C_{30}) alkyl radicals, and at most three of the radicals R_1 to R_4 are, independently of one another, hydrogen atoms, straight-chain or branched alkyl radicals or alkenyl radicals containing 1 to 30 carbon

atoms, aryl radicals such as, for example, phenyl radicals or naphthyl radicals, or aralkyl radicals such as, for example, benzyl radicals, it being possible for the aryl radicals and aralkyl radicals to be substituted on the aromatic ring by (C₁-C₃₀)alkyl, (C₁-C₃₀)alkoxy or hydroxyl groups or halogen atoms such as, for example, fluorine, chlorine, bromine or iodine atoms, and for two of the radicals R₁ to R₄ to join together to form a mono- or polycyclic ring system containing 4 to 12 carbon atoms which may be interrupted by 1 to 4 heteroatoms such as, for example, nitrogen, oxygen or sulfur atoms, and may contain 0 to 6 double bonds and also be substituted by fluorine, chlorine, bromine or iodine atoms, (C₁-C₆)alkyl, (C₁-C₆)alkoxy, nitro or amino groups, and X⁻ denotes an organic or inorganic anion, it being possible for the radicals R₁ to R₄ to be substituted by a COO⁻ or SO₃⁻ group and X⁻ ceasing in this case to be applicable, and of highly fluorinated immonium compounds of the formula (II)



in which R₉ to R₁₂ denote hydrogen atoms or organic radicals, at least one of the radicals R₉ to R₁₂ denoting a straight-chain or branched fluorine-containing alkyl radical or fluorine-containing alkenyl radical which contains 1 to 69 carbon atoms and 3 to 66 fluorine atoms and which may contain hydroxyl and/or chloromethyl and/or carboxamide and/or sulfonamide and/or urethane and/or amino and/or R₅-O-R₆ and/or R₇C(O)-O-R₈ groups in which R₅, R₆, R₇ and R₈ have the abovementioned meanings, and at most three of the radicals R₉ to R₁₂ denote, independently of one another, hydrogen atoms, straight-chain or branched alkyl radicals or alkenyl radicals containing 1 to 30 carbon atoms, aryl radicals such as, for example, phenyl radicals or naphthyl radicals, aralkyl radicals such as, for example, benzyl radicals, it being possible

for the aryl radicals or aralkyl radicals to be substituted on the aromatic ring by (C_1-C_{30}) alkyl, (C_1-C_{30}) alkoxy, hydroxyl groups or halogen atoms, and for two of the radicals R_9 to R_{12} to join together to form a mono-
5 or polycyclic ring system containing 4 to 17 carbon atoms which may be interrupted by 1 to 4 heteroatoms such as, for example, nitrogen, oxygen or sulfur atoms and may contain 2 to 9 double bonds and also be substituted by fluorine, chlorine, bromine or iodine atoms, a $(C_1-$
10 $C_6)$ alkyl, (C_1-C_6) alkoxy, nitro or amino group (in this case R_{12} becomes one of the abovementioned radicals on the ring), and Y^- is an organic or inorganic anion, it being possible for the radicals R_9 to R_{12} to be substituted by a COO^- or SO_3^- group and Y^- ceasing in this case
15 to be applicable, in a form in which they are incorporated homogenously into toners and developers, as colorless charge regulation agents having positive or negative regulation effect in said toners and developers for electrophotographic copying processes.

20 As organic or inorganic anion, X^- or Y^- may, for example, be Hal^- such as, for example, Cl^- , Br^- or I^- , and also PF_6^- , sulfate, phosphate, cyanate, thiocyanate, BF_4^- , $B(aryl)_4^-$ such as, for example, tetraphenyl borate, p-chlorotetraphenyl borate, p-methyltetraphenyl borate,
25 tetranaphthyl borate, and also phenolate, nitrophenolate, zinc tetracyanate, zinc tetrathiocyanate, $CH_3OSO_3^-$, saturated or unsaturated aliphatic or aromatic carboxylate or sulfonate such as, for example, acetate, lactate, benzoate, salicylate, 2-hydroxy-3-naphthoate, 2-
30 hydroxy-6-naphthoate, ethyl sulfonate, phenyl sulfonate, and also perfluorinated saturated or unsaturated aliphatic or aromatic carboxylate or sulfonate such as, for example, perfluoroacetate, perfluoroalkyl benzoate, perfluoroethyl sulfonate or perfluoroalkylbenzene
35 sulfonate.

The ammonium compounds and immonium compounds of the abovementioned formula (I) or (II) respectively may

[lacuna] on their own or in combination in toners or developers which are used for the electrophotographic copying or reproduction of originals and also for printing electronically, optically or magnetically stored information or in color-proofing. In addition, these compounds can be used for coating carriers and in powders and paints for surface coating, in particular in electrokinetically sprayed powder coatings, as charge improving agents.

10 Particularly suitable are compounds of the said formula (I) in which at least one of the radicals R_1 to R_4 denotes a straight-chain fluorine-containing alkenyl radical which contains 4 to 14 carbon atoms or a
15 straight-chain or branched fluorine-containing alkyl radical which contains 13 to 69 carbon atoms and which may contain hydroxyl and/or chloromethyl and/or carboxamide and/or urethane and/or amino and/or R_5 -O- R_6 groups in which R_5 and R_6 are (C_1 - C_{30})alkyl radicals, and
20 at most three of the radicals R_1 to R_4 are, independently of one another, hydrogen atoms, straight-chain or branched alkyl radicals containing 1 to 18 carbon atoms, and X^- is an organic or inorganic anion, it being possible for the radicals R_1 to R_4 to be substituted by a COO^- or SO_3^- group and X^- ceasing in this case to be
25 applicable.

Furthermore, compounds of the said formula (I) are particularly suitable in which two of the radicals R_1 to R_4 can join together to form a mono- or polycyclic ring system containing 4 to 10 carbon atoms which may be
30 interrupted by 1 to 4 heteroatoms such as, for example, nitrogen, oxygen or sulfur atoms and may contain 0 to 4 double bonds and also be substituted by fluorine, chlorine, bromine or iodine atoms, a (C_1 - C_6)alkyl, (C_1 - C_6)alkoxy, nitro or amino group, and at least one of
35 the radicals R_1 to R_4 denotes a straight-chain fluorine-containing alkenyl radical which contains 4 to 14 carbon atoms or a straight-chain or branched fluorine-containing

alkyl radical which contains 13 to 69 carbon atoms and which may contain hydroxyl and/or chloromethyl and/or carboxamide and/or urethane and/or amino and/or R_5-O-R_6 groups in which R_5 and R_6 are (C_1-C_{30}) alkyl radicals, and
5 at most one of the radicals R_1 to R_4 denotes a hydrogen atom, a straight-chain or branched alkyl radical containing 1 to 18 carbon atoms, and X^- denotes an organic or inorganic anion, it being possible for the radicals R_1 to R_4 to be substituted by a COO^- or SO_3^- group and X^-
10 ceasing in this case to be applicable.

Furthermore, compounds of the abovementioned formula (II) are particularly suitable in which at least one of the radicals R_9 to R_{12} denotes a straight-chain fluorine-containing alkenyl radical which contains 4 to 14 carbon
15 atoms or a straight-chain or branched fluorine-containing alkyl radical which contains 13 to 69 carbon atoms and which may contain hydroxyl and/or chloromethyl and/or carboxamide and/or urethane and/or amino and/or R_5-O-R_6 groups in which R_5 and R_6 are (C_1-C_{30}) alkyl radicals, and
20 at most three of the radicals R_9 to R_{12} denote, independently of one another, hydrogen atoms, straight-chain or branched alkyl radicals containing 1 to 18 carbon atoms, and Y^- denotes an organic or inorganic anion, it being possible for the radicals R_9 and R_{12} to be substituted by
25 a COO^- or SO_3^- group and Y^- ceasing in this case to be applicable.

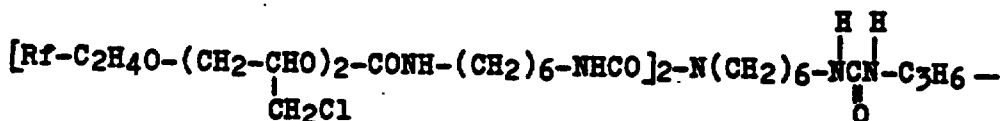
Furthermore, compounds of the abovementioned formula (II) in which two of the radicals R_9 to R_{12} can join together to form a mono- or polycyclic ring system containing 4 to
30 10 carbon atoms which may be interrupted by 1 to 4 heteroatoms such as, for example, nitrogen, oxygen or sulfur atoms and may contain 2 to 5 double bonds and also be substituted by fluorine, chlorine, bromine or iodine atoms, a (C_1-C_6) alkyl, (C_1-C_6) alkoxy, nitro or amino group
35 (in that case, R_{12} becomes one of the abovementioned substituents on the ring), and one of the radicals R_9 to R_{12} denotes a straight-chain fluorine-containing alkenyl

radical which contains 4 to 14 carbon atoms or a straight-chain or branched fluorine-containing alkyl radical which contains 13 to 69 carbon atoms and which may contain hydroxyl and/or chloromethyl and/or carboxamide and/or urethane and/or amino and/or R_5-O-R_6 groups in which R_5 and R_6 are (C_1-C_{30}) alkyl radicals, and Y^- is an organic or inorganic anion, it being possible for the radicals R_9 to R_{12} to be substituted by a COO^- or SO_3^- group and Y^- ceasing in this case to be applicable.

10 Quite particularly suitable are compounds of the abovementioned formula (I) in which at most three of the radicals R_1 to R_4 denote, independently of one another, a methyl, ethyl, stearyl, 2-hydroxyethyl or $-CH_2-CH_2-SO_3^-$ group (X^- ceases in the latter case to be applicable) and
15 at least one of the radicals R_1 to R_4 denotes one of the groupings



and

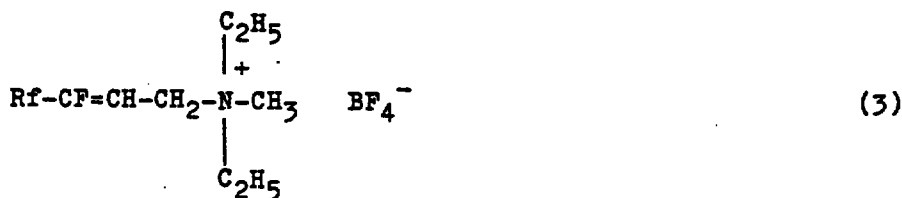
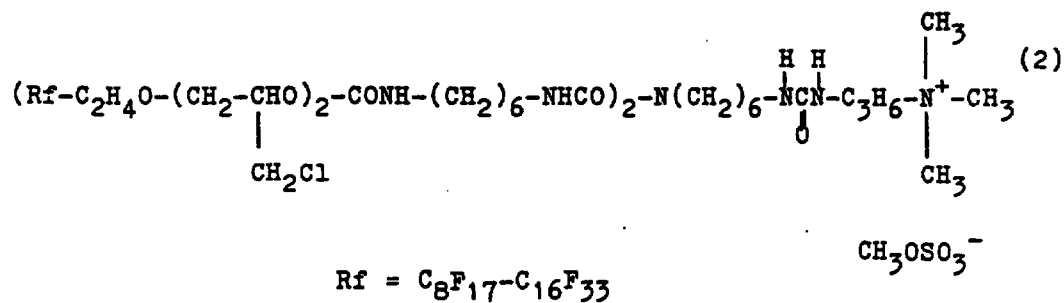
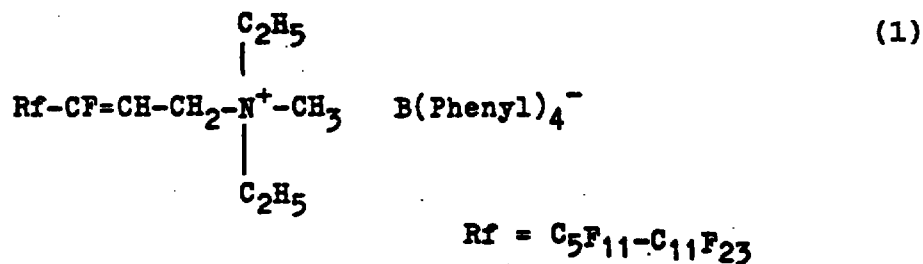


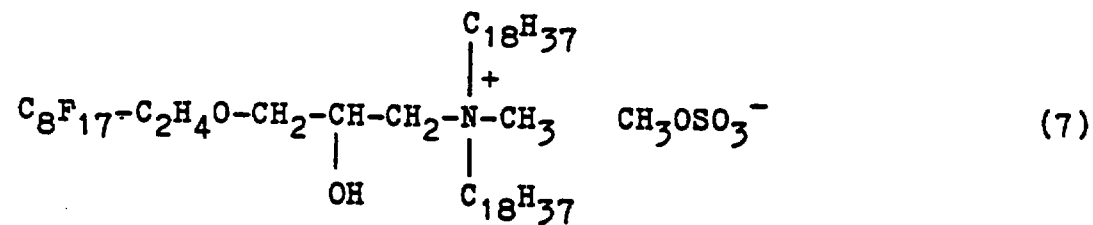
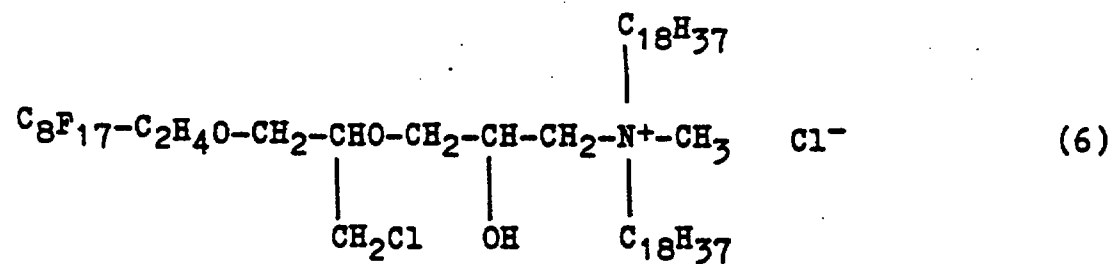
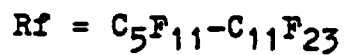
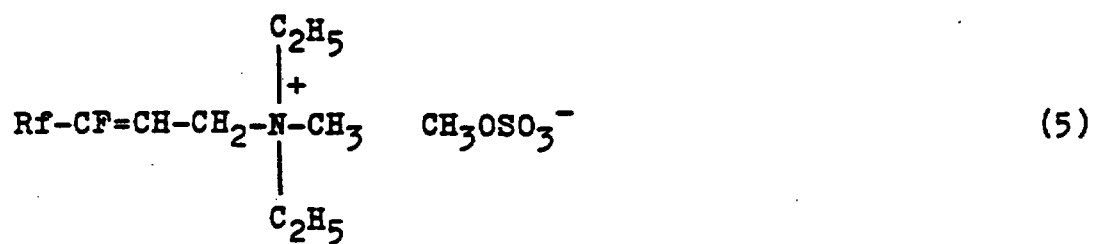
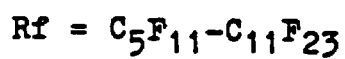
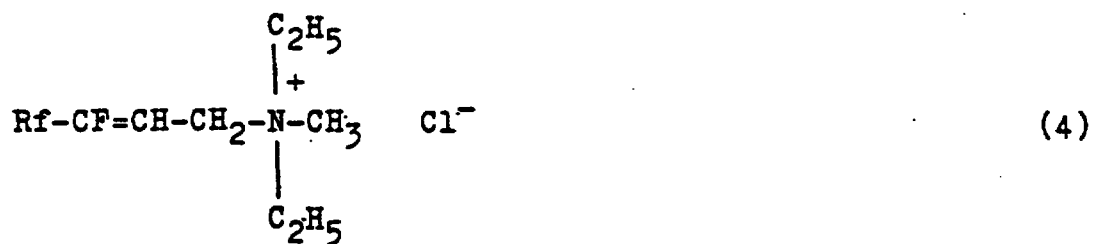
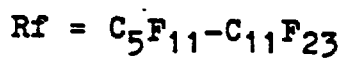
($Rf = C_8F_{17}-C_{16}F_{33}$), it being possible for two of the radicals R_1 to R_4 to join together to form a pyrroline, pyrrolidine, piperidine, morpholine or indoline ring, and
20 X^- being BF_4^- , Hal^- , for example Cl^- , Br^- or I^- , and also $CH_3-O-SO_3^-$, $B(aryl)_4^-$ such as, for example, tetraphenyl borate, p-chlorotetraphenyl borate, p-methyltetraphenyl borate or tetranaphthyl borate.

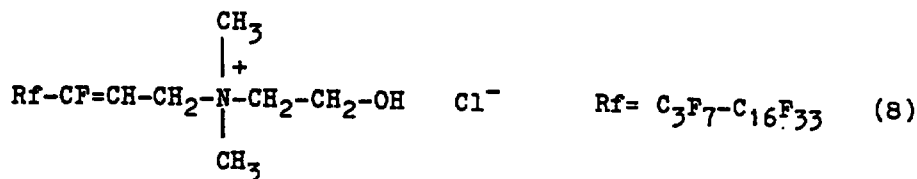
25 Of the compounds of the said formula (II) those are quite particularly suitable in which at least one of the radicals R_9 to R_{12} is a fluorine-containing alkyl radical which contains 1 to 14 carbon atoms and at most three of the radicals R_9 to R_{12} are, independently of one another,
30 methyl, ethyl, stearyl, 2-hydroxyethyl or $-CH_2-CH_2-SO_3^-$ groups (Y^- ceases in the latter case to be applicable),

it being possible for two of the radicals R_9 to R_{12} to join together to form a pyridine, pyrazine or quinoline ring, and R_{12} then being a fluorine, chlorine, bromine or iodine atom or a (C_1-C_6) alkyl, (C_1-C_6) alkoxy, nitro or amino group on the ring system, and X^- being BF_4^- , Hal^- such as, for example, Cl^- , Br^- or I^- , and also $CH_3-O-SO_3^-$, $B(aryl)_4^-$ such as, for example, tetraphenyl borate, chlorotetraphenyl borate, p-methyltetraphenyl borate or tetranaphthyl borate.

10 On individual compounds or compound mixtures of the said formulae (I) and (II) mention may be made, for example, of the following:







Thus, for example, a toner containing 0.5 to 1.0 percent by weight of compound (1) exhibits a charging of -4.0 or -21.7 $\mu\text{C/g}$ after 10 minutes and of -16.6 or -21.6 $\mu\text{C/g}$ after 24 hours of activation time (see Application Examples 1 and 2 of the Application Examples below).

A toner containing 2.5 percent by weight of the compound (2) has a chargeability of +6.0 $\mu\text{C/g}$ after 10 minutes and of +44.6 $\mu\text{C/g}$ after 24 hours of activation time (Application Example 3).

10 A toner containing 1.0 percent by weight of the compound (3) exhibits a chargeability of +13.4 $\mu\text{C/g}$ after 10 minutes and of +13.5 $\mu\text{C/g}$ after 24 hours of activation time (Application Example 4).

15 The compounds of the abovementioned formulae (I) and (II) may also be absorbed on suitable carrier materials such as, for example, silica gel, aluminum oxide, titanium dioxide from suitable media such as, for example, solvents. Thus, a toner containing 3.0 percent by weight of the compound (5) and absorbed on silica gel exhibits a
20 charging of +9.7 $\mu\text{C/g}$ after 10 minutes and of +16.2 $\mu\text{C/g}$

after 24 hours of activation time. Compared with the free compound (5), whose action in the toner collapses at high atmospheric humidity, absorption on silica gel consequently achieves an exceptional effectiveness of the compound (5) even at high atmospheric humidity (Application Example 6).

As already described above, pigments in toners are known to be able to affect the electrostatic charging of the toner severely. By way of examples, mention may be made here of the colorant C.I. Pigment Red 57:1 and C.I. Solvent Blue 125. C.I. Pigment Red 57:1 gives a toner a high negative charging with severe drift towards further increasing negative charging during prolonged activation time. C.I. Solvent Blue 125 produces a high positive charging in a toner which drops to almost zero during prolonged activation time as a result of severe drift. It is all the more surprising that, if 5 percent by weight of the colorant C.I. Pigment Red 57:1 or C.I. Solvent Blue 125 is incorporated along with 1 percent by weight of the compound (1) in a toner, the natural triboelectric effect of these colorants is fully compensated for by the high effectiveness of compound (1) and the required toner charging is established (Application Example 7 to 10).

If other ammonium compounds or immonium compounds are used instead of a compound according to the invention, the corresponding toners exhibit a much lower charging and, in some cases, charge reversal after prolonged activation time (Comparison Examples 1 and 2).

The compounds according to the invention are, as a rule, homogeneously incorporated in the respective carrier material in a concentration of about 0.01 to about 10% by weight, preferably about 0.1 to about 5.0% by weight, in a known manner, for example, by kneading in or extruding. In this connection, the charge regulation agents can be added as dried or ground powders, dispersions or solutions, press cakes, original batches, as compounds

absorbed on suitable carriers from aqueous or non-aqueous solution or in another suitable form. Equally, the compounds according to the invention can also in principle be added even during the preparation of the respective toner binders, i.e. in the course of the polymerization or polycondensation thereof. Typical toner binders are, for example, styrene resins, styrene acrylate resins, styrene butadiene resins, acrylate resins, polyester resins, amide resins, amine resins, ammonium resins, ethylene resins, phenolic resins or epoxy resins, individually or in combination, which may additionally contain further constituents such as pigments, waxes or flow promoters or which may have them added later.

The magnitude of the electrostatic charging of the electrophotographic toners in which the charge regulation agents claimed according to the invention have been homogeneously incorporated was measured using standard test systems under identical conditions (such as identical dispersion times, identical particle size distribution, identical particle shape) at room temperature and 50% relative atmospheric humidity and also at room temperature at 92% relative atmospheric humidity. For the measurement at 92% relative atmospheric humidity, the toner concerned was conditioned for 48 hours in a climatic chamber.

The toner in a two-component developer is activated by tumbling with a carrier (three parts by weight of toner to 97 parts by weight of carrier) on a roller mixer (150 revolutions per minute). Then the electrostatic charging is measured using a Q/M test bench (cf. J.H. Dessauer and H.E. Clark, "Xerography and related Processes", Focus Press, N.Y. 1965, page 289).

The particle size is of considerable influence in determining the Q/M value, and for this reason strict attention was paid to uniform particle size distribution in the toner samples obtained by sieving.

The Examples below serve to explain the invention without restricting it thereto. The parts referred to are parts by weight.

Preparation Example 1

5 160 ml of water are added to 40 ml of a 0.5 molar aqueous solution (0.020 mol) of the compound mixture of the formula (5) (molecular weight 672) mentioned further above and then 22 ml of a 1.0 M aqueous solution of sodium tetraphenyl borate (0.022 mol) are added dropwise
10 while stirring vigorously over a period of 15 to 20 minutes. The solution is made up to 500 ml with water and heated to 50°C and the thick white precipitate is filtered with suction while hot. The product is washed thoroughly with water and dried at 50°C in an air-
15 circulation oven.

Yield: 16.9 g (96.0% of theory) of the compound (1)

Molecular weight: 880

Melting point: 154-156°C

20 Elementary analysis: calc. 4.1% H, 1.6% N, 1.2% B
exp. 4.1% H, 1.6% N, 1.1% B, 0.05% water

¹H-NMR (in DMSO-d₆): 1.20 (triplet, 6 methyl-H),

2.97 (singlet, 3-methyl-H), 3.30 quartet, 4 ethyl-H),
25 4.25 (doublet, 2 allyl-H),
6.61 (doublet of triplets, 1 vinyl-H), 7.01 (multiplet, phenyl-H) ppm.
20

Preparation Example 2

30 The preparation of the compound (3) is carried out analogously to Preparation Example (1) using sodium tetrafluoroborate.

Yield: 12.3 g (95.0% of theory) of the compound (3)

Molecular weight: 648
Melting point: 202°C
Elementary analysis: calc. 2.5% H, 2.2% N, 1.7% B
exp. 2.7% H, 2.3% N, 1.8% B,
0.5% water
1H NMR (in DMSO-d6): 1.24 (triplet, 6 methyl-H)
3.02 (singlet, 3 methyl-H),
3.37 (quartet, 4 ethyl-H),
4.28 (doublet, 2 allyl-H),
6.63 (doublet of triplets, 1
vinyl-H) ppm.

Preparation Example 3

The compound (9) is prepared analogously to Preparation Example (1) using the corresponding perfluoroalkyl-pyridinium iodide and sodium tetraphenyl borate, and also isopropanol/water (1:1 parts by volume) as solvent.

Yield: 15.2 g (89.7 % of theory) of the compound (9)
Molecular weight: 845
Melting point: 163°C
Elementary analysis: calc. 55.4% C, 3.5% H, 1.7% N, 1.3% B 38.2% F
exp. 55.2% C, 3.3% H, 1.6%.N, 1.2% B, 36.8% F, 0.19% water
1H-NMR (in DMSO-d6): 3.25 (multiplet, 2 methylene-H),
4.97 (triplet, 2-methylene-H),
6.95 (multiplet, 20 phenyl-H),
8.62 (multiplet, 5-pyridyl-H) ppm.

Preparation Example 4

20 g of a 50% aqueous solution of the compound (5) are added to 20 g of silica gel ("Sipernat 22", manufactured by Degussa) and intimately mixed in a mixer. A fine, dry and readily free-flowing powder containing 25 percent by weight of the compound (5) is obtained.

The compounds (2) and also (4) to (8) were prepared analogously to US-PS 3,535,381, FR-PS 2,153,489, DE-A-1,922,277, DE-A-2,244,297, DE-A-3,606,933 and BE-PS 788,335, and the corresponding iodide as starting compound for the compounds (9) to (11) analogously to DE-A-1,922,277.

Application Example 1

0.5 parts of the compound (1) were homogeneously worked into 99.5 parts of toner binder (Dialec S 309 manufactured by Diamond Shamrock, styrene-methacrylate copolymer 60:40) for 45 minutes by means of a kneader manufactured by Werner & Pfleiderer (Stuttgart). Grinding was then carried out on the universal laboratory mill 100 LU (manufactured by Alpine, Augsburg) and classification was then carried out on a centrifugal classifier 100 MZR (manufactured by Alpine). The desired particle fraction (4-25 μm) was activated with a carrier of the type 90 (Xerographic Carrier manufactured by Plasma Materials Inc.) composed of magnetite particles 50 to 200 μm in size coated with styrene-methacrylate copolymer 90:10. The measurement was carried out using a standard Q/M test bench (manufactured by Epping GmbH, Neufahrn); a sieve having a mesh size of 25 μm (manufactured by Gebr. Kufferath, Düren) was used to ensure that it was not possible for carrier to be entrained while blowing out the toner. The following Q/M values ($\mu\text{C/g}$) were measured as a function of the activation time:

Activation time	Q/M ($\mu\text{C/g}$)	
	50% relative humidity	92%
10 min	-4.0	-0.6
30 min	-6.8	-4.1
2 h	-10.1	-9.7
24 h	-16.6	-16.5

Application Example 2

The procedure was as described in Application Example 1, with the difference that 1.0 part of the compound (1) was used in 99 parts of toner binder.

5	Q/M ($\mu\text{C/g}$)		
	Activation time	50% relative humidity	92%
10	10 min	-21.7	-16.3
	30 min	-22.5	-20.1
	2 h	-22.9	-20.9
	24 h	-21.6	-19.0

Application Example 3

The procedure was as described in Application Example 1 with the difference that 2.5 parts of the compound (2) were used in 95 parts of toner binder.

15	Q/M ($\mu\text{C/g}$)		
	Activation time	50% relative humidity	92%
20	10 min	+6.0	+3.0
	30 min	+9.6	+3.0
	2 h	+23.6	+1.3
	24 h	+44.6	+18.3

Application Example 4

The procedure was as described in Application Example 1, with the difference that 1.0 part of the compound (3) was used in 99 parts of toner binder.

		Q/M ($\mu\text{C/g}$)	
Activation time		50% relative humidity	92%
5	10 min	+13.4	+11.9
	30 min	+16.9	+15.7
	2 h	+17.5	+16.4
	24 h	+13.5	+15.9

Application Example 5

- 10 The procedure was as described in Application Example 1, with the difference that 1.0 part of the compound (4) was used in 99 parts of toner binder.

		Q/M ($\mu\text{C/g}$)	
Activation time		50% relative humidity	92%
15	10 min	+12.8	+13.0
	30 min	+15.5	+14.9
	2 h	+17.1	+17.1
	24 h	+16.8	+18.3
20			

Application Example 6

- 25 The procedure was as described in Application Example 1, with the difference that 3.0 parts of the compound (5) (in the form of 25 percent by weight of (5) on silica gel ("Sipernat 22", manufactured by Degussa) were used in 99 parts of toner binder and 6 parts of silica gel.

		Q/M ($\mu\text{C/g}$)	
Activation time		50% relative humidity	92%
30	10 min	+9.7	+12.0
	30 min	+11.9	+13.2
	2 h	+14.1	+13.9
	24 h	+16.2	+15.7

Application Example 7

5.0 parts of the colorant C.I. Pigment Red 57:1 were homogeneously worked into 95 parts of toner binder as described in Application Example 1.

5	Q/M ($\mu\text{C/g}$)	
	Activation time	50% relative humidity
10	10 min	-3.4
	30 min	-19.5
	2 h	-52.4
	24 h	-63.9

Application Example 8

5.0 parts of the colorant C.I. Solvent Blue 125 were homogeneously worked into 95 parts toner binder as described in Application Example 1.

15	Q/M ($\mu\text{C/g}$)	
	Activation time	50% relative humidity
20	10 min	+27.9
	30 min	+19.2
	2 h	+7.5
	24 h	+9.0

Application Example 9

1.0 part of the compound (1) and 5.0 parts of C.I. Pigment Red 57:1 were homogeneously worked into 94 parts of toner binder as described in Application Example 1.

Activation time	Q/M ($\mu\text{C/g}$)	
	50% relative humidity	92%
10 min	-19.6	-7.3
5 30 min	-22.1	-12.6
2 h	-26.3	-17.1
24 h	-23.3	-15.0

Application Example 10

- 10 1.0 part of the compound (1) and 5.0 parts of C.I. Solvent Blue 125 were homogeneously worked into 94 parts of toner binder as described in Application Example 1.

Activation time	Q/M ($\mu\text{C/g}$)	
	50% relative humidity	92%
10 min	-3.5	+0.7
30 min	-7.7	-2.0
2 h	-8.7	-5.3
24 h	-14.4	-10.0

Application Example 11

The procedure was as described in Application Example 1, with the difference that 1.0 part of the compound (9) was homogeneously worked into 99 parts of toner binder.

Activation time	Q/M ($\mu\text{C/g}$)	
	50% relative humidity	92%
10 min	-11.8	+3.7
30 min	-11.0	-5.9
30 2 h	-11.7	-4.4
24 h	-14.7	-8.0

Comparison Example 1

The procedure was as described in Application Example 1, with the difference that 1.0 part of cetylpyridinium chloride was homogeneously worked into 99 parts of toner binder.

Activation time	Q/M ($\mu\text{C/g}$)	
	50% relative humidity	
10 min	+12.6	
30 min	+7.6	
2 h	+0.9	
24 h	-9.7	

Comparison Example 2

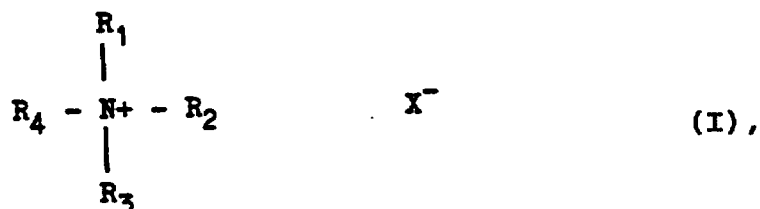
The procedure was as described in Application Example 1, with the difference that 1.0 part of benzyltrimethylammonium chloride was used in 99 parts of toner binder.

Activation time	Q/M ($\mu\text{C/g}$)	
	50% relative humidity	
10 min	+2.7	
30 min	-0.4	
2 h	-1.5	
24 h	-4.6	



Patent Claims

1. The use of highly fluorinated ammonium compounds of the formula (I)



- 5 in which R_1 to R_4 denote hydrogen atoms or organic radicals, at least one of the radicals R_1 to R_4 [lacuna] a straight-chain or branched fluorine-containing alkyl radical or fluorine-containing alkenyl radical which contains 1 to 69 carbon atoms and 3 to 66 fluorine atoms and which may contain hydroxyl and/or chloromethyl and/or carboxamide and/or sulfonamide and/or urethane and/or amino and/or R_5-O-R_6 and/or $R_7-C(O)-O-R_8$ groups in which R_5 , R_6 , R_7 and R_8 are (C_1-C_{30}) alkyl radicals, and at most three of the radicals R_1 to R_4 are, independently of one another, hydrogen atoms, straight-chain or branched alkyl radicals or alkenyl radicals containing 1 to 30 carbon atoms, aryl radicals or aralkyl radicals which may be substituted by (C_1-C_{30}) alkyl, (C_1-C_{30}) alkoxy or hydroxyl groups or halogen atoms, it being possible for two of the radicals R_1 to R_4 to join together to form a mono- or polycyclic ring system containing 4 to 12 carbon atoms which may be interrupted by 1 to 4 heteroatoms and may contain 0 to 6 double bonds and also be substituted by fluorine, chlorine, bromine or iodine atoms, (C_1-C_6) alkyl, (C_1-C_6) alkoxy, nitro or amino groups, and X^- denotes an organic or inorganic anion, it being possible for the radicals R_1 to R_4 to be substituted by a COO^- or SO_3^- group and X^- ceasing in this case to be applicable, and of highly fluorinated iminium compounds of the formula (II)



in which R_9 to R_{12} denote hydrogen atoms or organic radicals, at least one of the radicals R_9 to R_{12} denoting a straight-chain or branched fluorine-containing alkyl radical or fluorine-containing alkenyl radical which contains 1 to 69 carbon atoms and 3 to 66 fluorine atoms and which may contain hydroxyl and/or chloromethyl and/or carboxamide and/or sulfonamide and/or urethane and/or amino and/or R_5 -O- R_6 and/or R_7 C(O)-O- R_8 groups in which R_5 , R_6 , R_7 and R_8 have the abovementioned meanings, and at most three of the radicals R_9 to R_{12} denote, independently of one another, hydrogen atoms, straight-chain or branched alkyl radicals or alkenyl radicals containing 1 to 30 carbon atoms, aryl radicals or aralkyl radicals, it being possible for the aryl radicals or aralkyl radicals to be substituted on the aromatic ring by (C_1-C_{30}) alkyl, (C_1-C_{30}) alkoxy, hydroxyl groups or halogen atoms, and for two of the radicals R_9 to R_{12} to join together to form a mono- or polycyclic ring system containing 4 to 17 carbon atoms which may be interrupted by 1 to 4 heteroatoms and may contain 2 to 9 double bonds and also be substituted by fluorine, chlorine, bromine or iodine atoms, (C_1-C_6) alkyl, (C_1-C_6) alkoxy, nitro or amino groups, and Y^- is an organic or inorganic anion, it being possible for the radicals R_9 to R_{12} to be substituted by a COO^- or SO_3^- group and Y^- ceasing in this case to be applicable, in a form in which they are incorporated homogeneously into toners and developers, as colorless charge regulation agents having positive or negative regulation effect in said toners and developers for electrophotographic recording processes.



2. The use of highly fluorinated ammonium compounds as claimed in claim 1, wherein, in the formula (I) mentioned in claim 1, at least one of the radicals R_1 to R_4 denotes a straight-chain fluorine-containing alkenyl radical which contains 4 to 14 carbon atoms or a straight-chain or branched fluorine-containing alkyl radical which contains 13 to 69 carbon atoms and which may contain hydroxyl and/or chloromethyl and/or carboxamide and/or urethane and/or amino and/or R_5 -O- R_6 groups in which R_5 and R_6 are (C_1 - C_{30})alkyl radicals, and at most three of the radicals R_1 to R_4 are, independently of one another, hydrogen atoms, straight-chain or branched alkyl radicals containing 1 to 18 carbon atoms, and X^- is an organic or inorganic anion, it being possible for the radicals R_1 to R_4 to be substituted by a COO^- or SO_3^- group and X^- ceasing in this case to be applicable.
3. The use of highly fluorinated ammonium compounds as claimed in claim 1, wherein, in the formula (I) mentioned in claim 1, two of the radicals R_1 to R_4 form a mono- or polycyclic ring system containing 4 to 10 carbon atoms which may be interrupted by 1 to 4 heteroatoms and may contain 0 to 4 double bonds and also be substituted by fluorine, chlorine, bromine or iodine atoms, (C_1 - C_6)alkyl, (C_1 - C_6)alkoxy, nitro or amino groups, and at least one of the radicals R_1 to R_4 denotes a straight-chain fluorine-containing alkenyl radical which contains 4 to 14 carbon atoms or a straight-chain or branched fluorine-containing alkyl radical which contains 13 to 69 carbon atoms and which may contain hydroxyl and/or chloromethyl and/or carboxamide and/or urethane and/or amino and/or R_5 -O- R_6 groups in which R_5 and R_6 are (C_1 - C_{30})alkyl radicals, and at most one of the radicals R_1 to R_4 denotes a hydrogen atom, a straight-chain or branched alkyl radical containing 1 to 18 carbon atoms, and X^- denotes an organic or



inorganic anion, it being possible for the radicals R_1 to R_4 to be substituted by a COO^- or SO_3^- group and X^- ceasing in this case to be applicable.

4. The use of highly fluorinated iminium compounds as claimed in claim 1, wherein, in the formula (II) mentioned in claim 1, at least one of the radicals R_9 to R_{12} denotes a straight-chain fluorine-containing alkenyl radical which contains 4 to 14 carbon atoms or a straight-chain or branched fluorine-containing alkyl radical which contains 13 to 69 carbon atoms and which may contain hydroxyl and/or chloromethyl and/or carboxamide and/or urethane and/or amino and/or $R_5\text{-O-}R_6$ groups in which R_5 and R_6 are $(C_1\text{-}C_{30})$ alkyl radicals, and at most three of the radicals R_9 to R_{12} denote, independently of one another, hydrogen atoms, straight-chain or branched alkyl radicals containing 1 to 18 carbon atoms, and Y^- denotes an organic or inorganic anion, it being possible for the radicals R_9 and R_{12} to be substituted by a COO^- or SO_3^- group and Y^- ceasing in this case to be applicable.
5. The use of highly fluorinated iminium compounds as claimed in claim 1, wherein, in the formula (II) mentioned in claim 1, two of the radicals R_9 to R_{12} form a mono- or polycyclic ring system containing 4 to 10 carbon atoms which may be interrupted by 1 to 4 heteroatoms from the series nitrogen, sulfur or oxygen and may contain 2 to 5 double bonds and be substituted by fluorine, chlorine, bromine or iodine atoms, $(C_1\text{-}C_6)$ alkyl, $(C_1\text{-}C_6)$ alkoxy, nitro or amino groups, and at least one of the radicals R_9 to R_{12} denotes a fluorine-containing alkenyl radical which contains 4 to 14 carbon atoms or a straight-chain or branched fluorine-containing alkyl radical which contains 13 to 69 carbon atoms and which may contain hydroxyl and/or chloromethyl and/or carboxamide and/or urethane and/or amino and/or $R_5\text{-O-}R_6$ groups



in which R_5 and R_6 are (C_1-C_{30}) alkyl radicals, and Y^- is an organic or inorganic anion, it being possible for the radicals R_9 to R_{12} to be substituted by a COO^- or SO_3^- group and Y^- ceasing in this case to be applicable.

5

6. The use of highly fluorine-containing ammonium compounds or iminium compounds as claimed in claim 1, wherein, in the formulae (I) and (II) mentioned therein, X^- and Y^- denote Cl^- , Br^- , I^- , PF_6^- , sulfate, phosphate, cyanate, thiocyanate, BF_4^- , tetraphenylborate, p-chlorotetraphenylborate, p-methyltetraphenylborate, tetranaphthyl borate, phenolate, nitrophenolate, zinc tetracyanate, zinc tetrathiocyanate, $CH_3OSO_3^-$, saturated or unsaturated aliphatic or aromatic carboxylate or sulfonate, perfluorinated saturated or unsaturated aliphatic or aromatic carboxylate or sulfonate.

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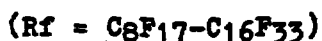
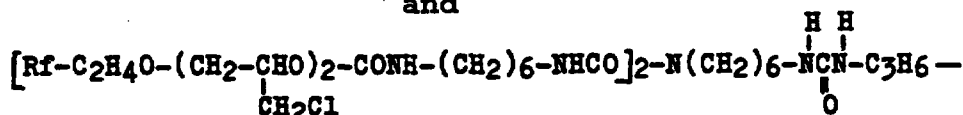
7. The use of highly fluorinated ammonium compounds as claimed in claim 1, wherein, in the formula (I) mentioned in claim 1, at most three of the radicals R_1 to R_4 denote, independently of one another, a methyl, ethyl, stearyl, 2-hydroxyethyl or $-CH_2-CH_2-SO_3^-$ group (X^- ceases in the latter case to be applicable) and at least one of the radicals R_1 to R_4 denotes one of the groupings

20

25



and



it being possible for two of the radicals R_1 to R_4 to form a pyrroline, pyrrolidine, piperidine, morpholine or indoline ring, and X^- being BF_4^- , Cl^- , Br^- , I^- , $CH_3-O-SO_3^-$, tetraphenylborate, p-chloro-tetraphenylborate, p-methyltetraphenylborate or

30



tetranaphthylborate.

8. The use of highly fluorinated iminium compounds as claimed in claim 1, wherein, in the formula (II) mentioned in claim 1, at least one of the radicals R_9 to R_{12} is a fluorine-containing alkyl radical which contains 1 to 14 carbon atoms and at most three of the radicals R_9 to R_{12} are, independently of one another, methyl, ethyl, stearyl, 2-hydroxyethyl or $-\text{CH}_2-\text{CH}_2-\text{SO}_3^-$ groups (Y⁻ ceases in the latter case to be applicable), it being possible for two of the radicals R_9 to R_{12} to form a pyridine, pyrazine or quinoline ring, and R_{12} then being a fluorine, chlorine, bromine or iodine atom or a (C_1-C_6) alkyl, (C_1-C_6) alkoxy, nitro or amino group on the ring system, and X⁻ being BF_4^- , Cl^- , Br^- , I^- , $\text{CH}_3-\text{O}-\text{SO}_3^-$, tetraphenylborate, chlorotetraphenylborate, p-methyltetraphenylborate or tetranaphthylborate.
9. The use of ammonium compounds or iminium compounds mentioned in at least one of claims 1 to 8, individually or in combination, to prepare toners or developers which are used for the electrophotographic copying or reproduction of originals and also for printing electronically, optically or magnetically stored information or in color-proofing.
10. The use of ammonium compounds or iminium compounds mentioned in at least one of claims 1 to 8, wherein the ammonium compounds or iminium compounds, individually or in combination, are used in a concentration of about 0.01 to about 10 percent by weight.
11. The use of ammonium compounds or iminium compounds mentioned in at least one of claims 1 to 8, individually or in combination and in homogeneous mixture with a toner binder, to coat carriers which are used in developers for the electrophotographic



copying or reproduction of originals and also for printing electronically, optically or magnetically stored information or in color-proofing.

- 5 12. The use of ammonium compounds or iminium compounds mentioned in at least one of claims 1 to 8, individually or in combination, as charge improving agent in powders and paints for the surface coating of objects made of metal, wood, plastic, glass, ceramic, concrete, textile material, paper or
10 rubber, in particular in electrokinetically sprayed powder coatings.