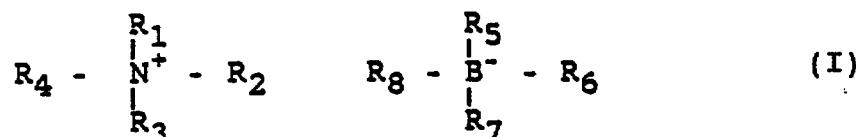


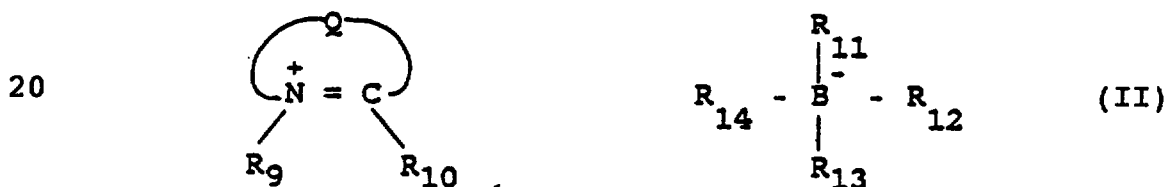
Description

The present invention relates to novel ammonium and iminium compounds and processes for their preparation.

The present invention specifically relates to novel ammonium compounds of the general formula (I)



in which at least one of the radicals R_1 to R_4 denotes a straight-chain fluorine-containing unsaturated and/or saturated alkyl radical having 4 to 30 carbon atoms and not more than three of the radicals R_1 to R_4 independently of one another denote hydrogen atoms or straight-chain or branched alkyl or hydroxyalkyl radicals having 1 to 30 carbon atoms, and R_5 to R_8 denote aryl radicals, such as, for example, phenyl or naphthyl radicals, and furthermore alkylaryl radicals, such as, for example, the toluyl radical, halogenoaryl radicals, such as, for example, fluorophenyl or chlorophenyl radicals, or fluorine atoms, and to mixtures of these compounds, and iminium compounds of the general formula (II)



(+)
in which Q, together with the constituent $-N=C-$, forms a mono- or polynuclear ring system having 4 to 17 carbon atoms, which can additionally be interrupted by 1 to 4 hetero atoms, such as, for example, nitrogen, oxygen or sulfur atoms, and contain 2 to 9 double bonds, and which can be substituted in any desired position by fluorine, chlorine, bromine or iodine atoms or alkyl(C_1-C_6), alkoxy(C_1-C_6), nitro or amino groups, R_9 denotes a fluorine-containing alkyl(C_1-C_{30}) radical, R_{10} denotes a hydrogen,

fluorine, chlorine, bromine or iodine atom or an alkyl-
(C₁-C₈), alkoxy(C₁-C₈), nitro or amino group and the
radicals R₁₁ to R₁₄ denote aryl radicals, such as, for
example, phenyl or naphthyl radicals, alkylaryl radicals,
5 such as, for example, the toluyyl radical, halogenoaryl
radicals, such as, for example, fluorophenyl or chloro-
phenyl radicals, or fluorine atoms, and to mixtures of
these compounds.

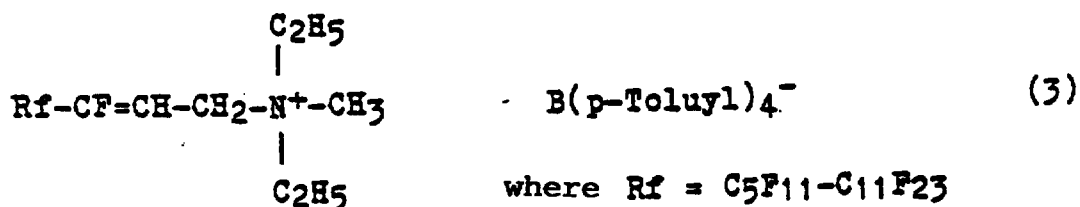
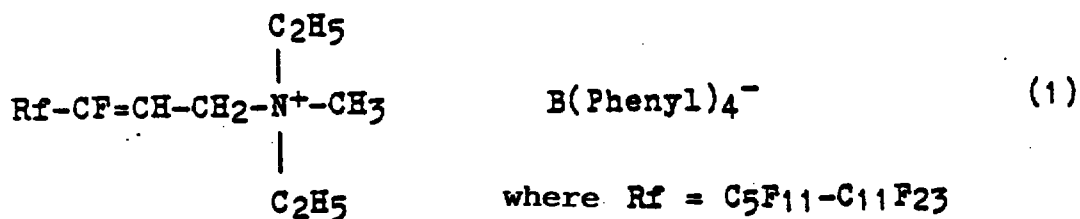
10 The invention particularly relates to those compounds of
the abovementioned general formula (I) in which at least
one of the radicals R₁ to R₄ denotes a straight-chain
fluorine-containing unsaturated and/or saturated alkyl
radical having 4 to 14 C atoms and not more than three of
the radicals R₁ to R₄ independently of one another denote
15 straight-chain or branched alkyl(C₁-C₄) or hydroxyalkyl-
(C₁-C₄) radicals, and R₅ to R₈ denote phenyl, naphthyl, p-
chlorophenyl or p-toluyyl radicals or fluorine atoms, and
to compounds of the general formula (II) mentioned, in
20 which Q, together with the constituent ⁽⁺⁾-N=C-, forms a
mono- or polynuclear ring system having 4 to 10 carbon
atoms, which can additionally be interrupted by 1 to 4
hetero atoms, such as, for example, nitrogen, oxygen or
sulfur atoms, and contain 2 to 5 double bonds and which
25 can be substituted in any desired position by fluorine,
chlorine, bromine or iodine atoms or alkyl(C₁-C₈), alkoxy-
(C₁-C₈), nitro or amino groups, R₉ denotes a fluorine-
containing alkyl(C₄-C₁₄) radical, R₁₀ denotes a hydrogen,
fluorine, chlorine, bromine or iodine atom or an alkyl-
30 (C₁-C₈), alkoxy(C₁-C₈), nitro or amino group and the
radicals R₅ to R₈ and R₁₁ to R₁₄ denote phenyl, p-chloro-
phenyl, p-toluyyl or naphthyl radicals or fluorine atoms,
and to mixtures of these compounds.

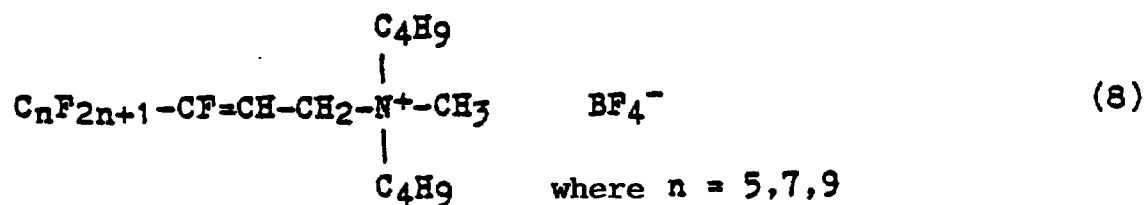
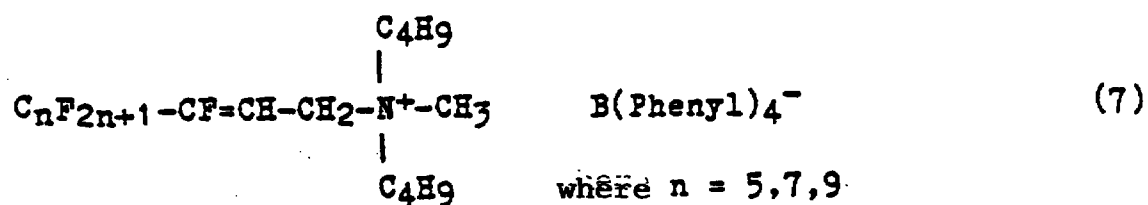
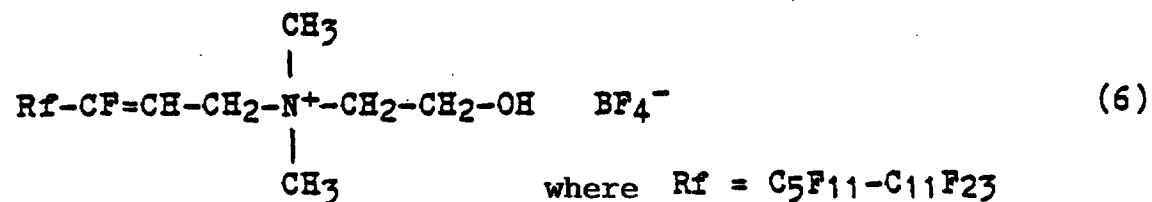
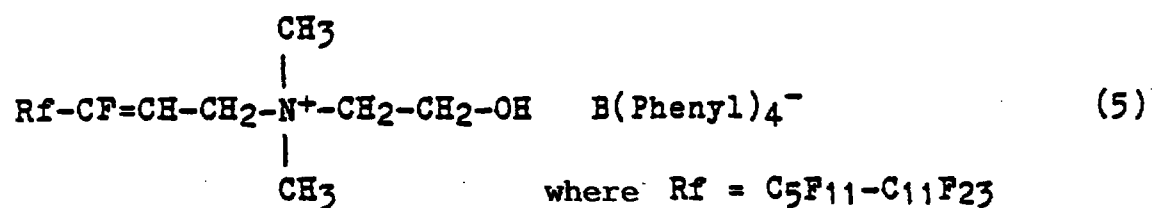
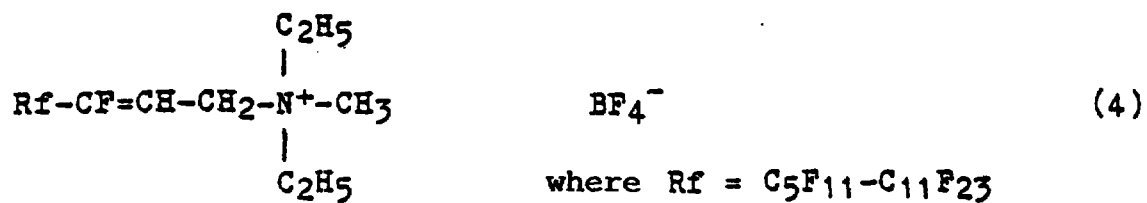
35 The invention especially relates to compounds of the
abovementioned general formula (I) in which at least one
of the radicals R₁ to R₄ denotes the group -CH₂-CH=CF-Rf
(Rf = C₅F₁₁-C₁₁F₂₃), the group -CH₂-CH=CF-C_nF_{2n+1}, where

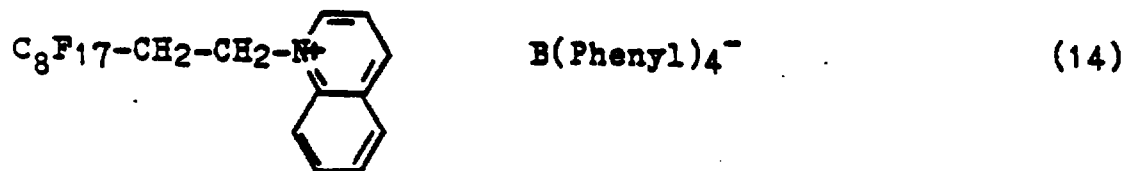
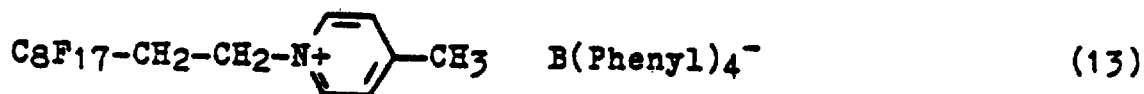
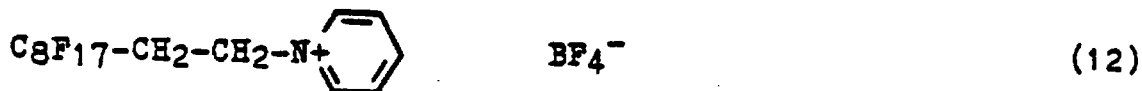
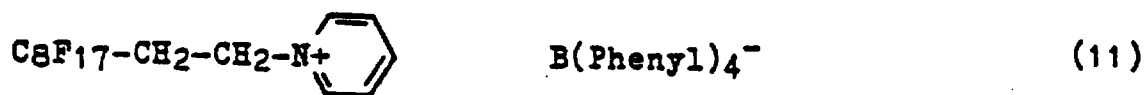
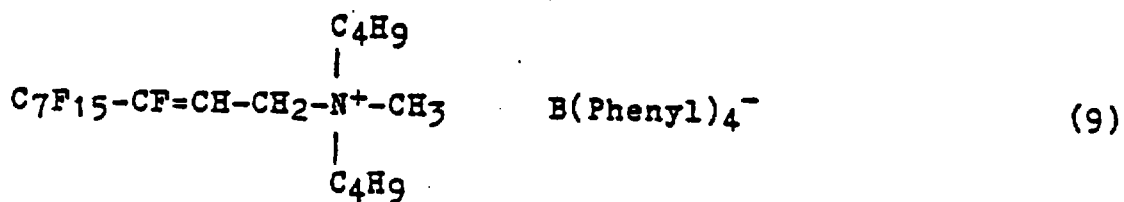
n = 5, 7 or 9, or the group $-\text{CH}_2-\text{CH}=\text{CF}-\text{C}_7\text{F}_{15}$, and not more than three of the radicals R_1 to R_4 independently of one another denote a methyl, ethyl, butyl or hydroxyethyl group, and to compounds of the abovementioned general formula (II) in which Q, together with the constituent

(+)
-N=C- forms a pyridine, pyrazine or quinoline ring system, R_9 denotes a $\text{C}_8\text{F}_{17}-\text{CH}_2-\text{CH}_2-$ group, R_{10} denotes a hydrogen atom and the radicals R_5 to R_8 and R_{11} to R_{14} denote phenyl, p-chlorophenyl, p-toluy1 or naphthyl radicals or fluorine atoms, and to mixtures of these compounds.

The following may be mentioned as examples of individual compounds or mixtures of compounds of the general formulae (I) or (II):







The ammonium or iminium compounds and mixtures of ammonium or iminium compounds of the general formulae (I) or (II) mentioned can be prepared by reacting the ammonium compounds and mixtures of ammonium compounds of the general formula (III)



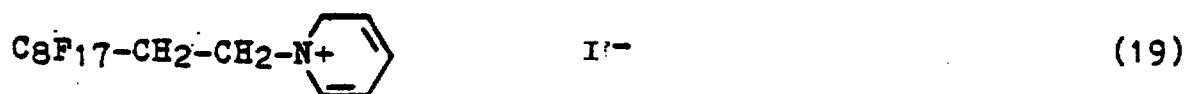
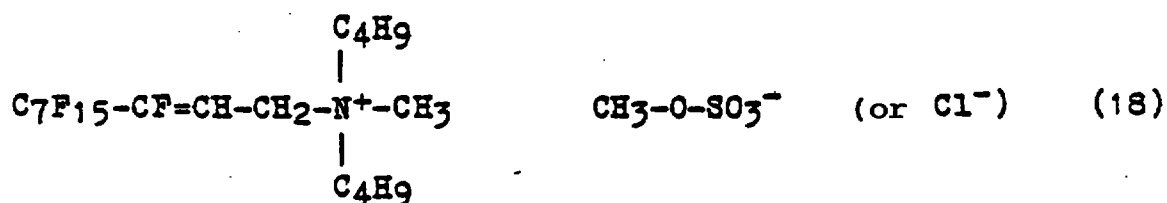
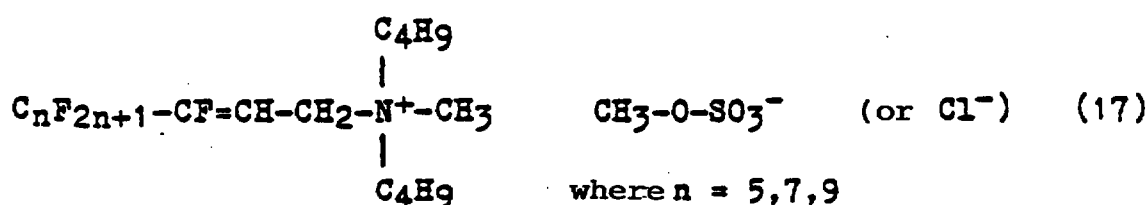
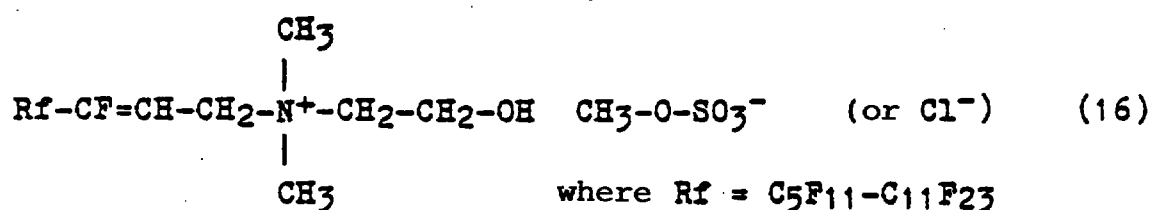
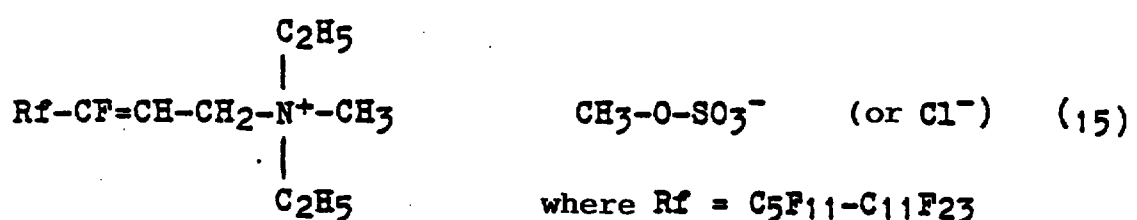
in which at least one of the radicals R_1 to R_4 denotes a straight-chain fluorine-containing unsaturated and/or saturated alkyl radical having 4 to 30 carbon atoms and not more than three of the radicals R_1 to R_4 independently of one another denote hydrogen atoms or straight-chain or branched alkyl or hydroxyalkyl radicals having 1 to 30 carbon atoms, and X^- denotes a halogen anion, for example a chlorine, bromine or iodine anion, or a methylsulfate anion, and by reacting iminium compounds or mixtures of iminium compounds of the general formula (IV)



in which Q, together with the constituent $\text{N}^+=\text{C}^{(+)}$, forms a mono- or polynuclear ring system having 4 to 17 carbon atoms, which can additionally be interrupted by 1 to 4 hetero atoms, preferably nitrogen, oxygen or sulfur atoms, and contain 2 to 9 double bonds, and which can be substituted in any desired position by fluorine, chlorine, bromine or iodine atoms or an alkyl(C_1-C_6), alkoxy(C_1-C_6), nitro or amino group, R_9 denotes a fluorine-containing alkyl(C_1-C_{30}) radical, R_{10} denotes a hydrogen, fluorine, chlorine, bromine or iodine atom or an alkyl(C_1-C_6), alkoxy(C_1-C_6), nitro or amino group and Y^- denotes a halogen anion, for example a chlorine, bromine or iodine anion, or a methylsulfate anion (the synthesis of the compounds of the general formulae III and IV mentioned is described in U.S. Patent No.3,535,381, German Offenlegungsschrift 1,922,277, German Offenlegungsschrift 2,244,297 and German Offenlegungsschrift 3,306,933), with a borate salt in water or mixtures of water and organic solvent, such as, for example, isopropanol, isobutanol or methyl isobutyl ketone, at temperatures from about 20°C to about 90°C , preferably from about 50°C to about 80°C .

The compounds and compound mixtures of the general formulae (I) and (II) are obtained in a good yield and purity by this process and can be isolated directly from the reaction medium by filtration.

- 5 Thus, for example, the above compounds of the formulae (1) to (14) are prepared by reacting the starting compounds (15) to (21) below





with sodium tetraphenylborate, sodium tetra-p-chloro-phenylborate, sodium tetra-p-toluyllborate or sodium tetrafluoroborate (see the following Preparation Examples 1 to 6). Sodium tetra-p-chlorophenylborate and sodium
5 tetra-p-toluyllborate were prepared in accordance with the instructions of H.Holzapfel and C. Richter, J. Prakt. Chem. 26 (1964), 15-23. The ammonium and iminium compounds according to the invention are outstandingly
10 suitable for use as charge control agents in electrophotographic toners and developers for electrophotographic recording processes.

The preparation examples below serve to illustrate the invention without limiting it to these.

Preparation Example 1

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

25 Yield: 16.9 g (96.0% of theory) of the compound (1)
Molecular weight: 880
Melting point: 154-156°C

Elemental analysis: calculated 4.1% H, 1.6% N, 1.2% B
found 4.1% H, 1.6% N, 1.1% B,
0.05% water

5 1H-NMR(in DMSO-d6): 1.20 (triplet, 6 methyl-H), 2.97
(singlet, 3 methyl-H), 3.30
(quartet, 4 methylene-H), 4.25
(doublet, 2 allyl-H), 6.61
(doublet of triplets, 1 vinyl-H),
7.01 (multiplet, 20 phenyl-H) ppm.

10 Preparation Example 2

The procedure was as described in Preparation Example 1,
with the difference that sodium tetra-p-chloro-phenyl-
borate was used instead of sodium tetraphenylborate.

15 Yield: 15.4 g (75.6% of theory) of the
compound of the abovementioned
formula (2)

Molecular weight: 1018

Melting point: 63-64°C

20 Elemental analysis: calculated 3.1% H, 1.4% N, 1.1% B,
13.9% Cl,
found 3.4% H, 1.5% N, 1.1% B,
14.5% Cl, 0.07% H₂O

25 1H-NMR(in DMSO-d6): 1.23 (triplet, 6 methyl-H), 3.01
(singlet, 3 methyl-H), 3.36 (quar-
tet, 4 methylene-H), 4.28 (doublet,
2 allyl-H), 6.63 (doublet of trip-
lets, 1 vinyl-H), 7.04 (multiplet,
16 p-chlorophenyl-H) ppm.

Preparation Example 3

30 The procedure was as described in Preparation Example 1,
with the difference that sodium tetra-p-toluyllborate was
employed instead of sodium tetraphenylborate and the
solvent was replaced by isopropanol/water (1:1 parts by

volume).

Yield: 11.5 g (61.2% of theory) of the compound of the abovementioned formula (3)

- 5 Molecular weight: 936
Melting point: 151-152°C
Elemental analysis: calculated 4.7% H, 1.5% N, 1.2% B
found 5.0% H, 1.9% N, 1.2% B, 0.07% H₂O
- 10 ¹H-NMR (in DMSO-d₆): 1.21 (triplet, 6 methyl-H), 2.15 (singlet, 3 toluylmethyl-H), 2.97 (singlet, 3 methyl-H), 3.33 (quartet, 4 methylene-H), 4.23 (doublet, 2 allyl-H), 6.60 (partly overlapped doublet of triplets, 1 vinyl-H), 6.88 (multiplet, 16 p-toluy-H) ppm.
- 15

Preparation Example 4

- The procedure was as described in Preparation Example 1, with the difference that sodium tetrafluoroborate was employed instead of sodium tetraphenylborate.
- 20

- Yield: 12.3 g (95.0% of theory) of the compound of the abovementioned formula (4)
- 25 Molecular weight: 648
Melting point: 202°C
Elemental analysis: calculated 2.5% H, 2.2% N, 1.7% B
found 2.7% H, 2.3% N, 1.8% B, 0.5% water
- 30 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 5

7.8 g (0.012 mol) of the compound (19) are dissolved in 200 ml of hot isobutanol. 100 ml of water are then added and 4.1 g (0.012 mol) of sodium tetraphenylborate are then slowly added, while stirring. The mixture is stirred vigorously for 1 hour and the product is then filtered off with suction, washed with isobutanol/water (1:1 parts by volume) and then with water and dried at 50°C in vacuo.

10 Yield: 9.1 g (89.7% of theory) of the compound of the abovementioned formula (11)

Molecular weight: 845

Melting point: 163°C

15 Elemental analysis: calculated 55.4% C, 3.5% H, 1.7% N, 1.3% B, 38.2% F
found 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),
20 4.97 (triplet, 2 methylene-H),
7.00 (multiplet, 20 phenyl-H),
8.59 (multiplet, 5 pyridyl-H) ppm.

Preparation Example 6

11.1 g (0.017 mol) of the compound of the abovementioned formula (19) are dissolved in 400 ml of hot water, and 1.9 g (0.017 mol) of sodium tetrafluoroborate are then slowly added, while stirring. The mixture is stirred vigorously for 1 hour, the product is filtered off hot with suction, washed with hot water and dried at 50°C in vacuo.

Yield: 8.7 g (83.5% of theory) of the compound of the abovementioned formula (12)

Molecular weight: 613

Melting point: 169°C

Elemental analysis: calculated 29.4% C, 1.5% H, 2.3% N,
1.8% B

5 found 29.5% C, 1.6% H, 2.4% N,
1.5% B, 0.06% H₂O

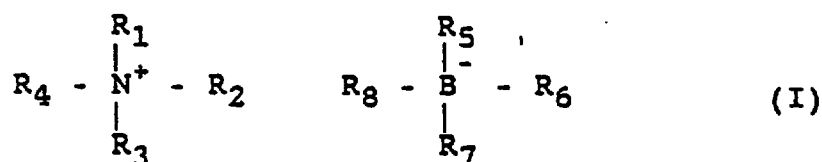
¹H-NMR (in DMSO-d₆): 3.21 (multiplet, 2 methylene-H),
5.03 (triplet, 2 methylene-H),
8.64 (multiplet, 5 pyridyl-H) ppm.

10 The individual compounds and compound mixtures of the
abovementioned formulae (5) to (10) and (13) and (14)
were obtained analogously.

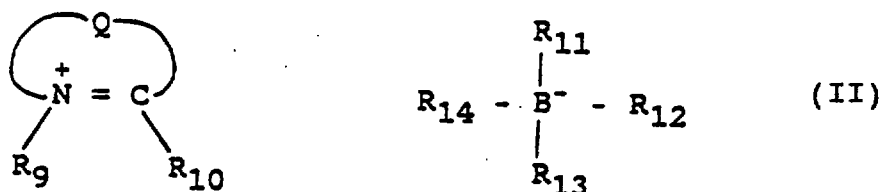


PATENT CLAIMS

1. An ammonium compound of the formula (I)



- 5 in which at least one of the radicals R_1 to R_4 denotes a straight-chain fluorine-containing unsaturated and/or saturated alkyl radical having 4 to 30 carbon atoms and not more than three of the radicals R_1 to R_4 independently of one another denote hydrogen atoms or straight-chain or branched alkyl or hydroxyalkyl radicals having 1 to 30
10 carbon atoms, and R_5 to R_8 denote aryl, alkylaryl or halogenoaryl radicals or fluorine atoms, or an iminium compound of the formula (II)



- 15 in which Q, together with the constituent $\text{N}^+ = \text{C}^-$, forms a mono- or polynuclear ring system having 4 to 17 carbon atoms, which can additionally be interrupted by 1 to 4 hetero atoms and contain 2 to 9 double bonds, and which can be substituted in any desired position by fluorine,
20 chlorine, bromine or iodine atoms or alkyl($\text{C}_1\text{-C}_6$), alkoxy($\text{C}_1\text{-C}_6$), nitro or amino groups, R_9 denotes a fluorine-containing alkyl($\text{C}_1\text{-C}_{30}$) radical, R_{10} denotes a hydrogen, fluorine, chlorine, bromine or iodine atom or an alkyl-
25 ($\text{C}_1\text{-C}_6$), alkoxy($\text{C}_1\text{-C}_6$), nitro or amino group and the radicals R_{11} to R_{14} denote aryl radicals, alkylaryl radicals, halogenoaryl radicals or fluorine atoms, or a mixture of these compounds.

2. A compound of the formula (I) as claimed in claim 1, in which at least one of the radicals R_1 to R_4 denotes a

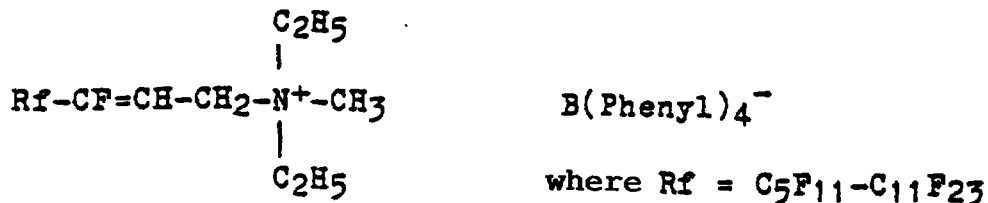


straight-chain fluorine-containing unsaturated and/or saturated alkyl radical having 4 to 14 carbon atoms and not more than three of the radicals R_1 to R_4 independently of one another denote straight-chain or branched alkyl-
5 (C_1-C_4) or hydroxyalkyl (C_1-C_4) radicals, and R_5 to R_8 denote phenyl, naphthyl, p-chlorophenyl, p-toluyll radicals or fluorine atoms, or a compound of the formula (II) mentioned in claim 1, in which Q, together with the
10 constituent $\overset{(+)}{-N=C-}$, forms a mono- or polynuclear ring system having 4 to 10 carbon atoms, which can additionally be interrupted by 1 to 4 hetero atoms and contain 2 to 5 double bonds and which can be substituted
15 in any desired position by fluorine, chlorine, bromine or iodine atoms or alkyl (C_1-C_6) , alkoxy (C_1-C_6) , nitro or amino groups, R_9 denotes a fluorine-containing alkyl (C_4-C_{14}) radical, R_{10} denotes a hydrogen, fluorine, chlorine, bromine or iodine atom or an alkyl (C_1-C_6) , alkoxy (C_1-C_6) , nitro or amino group and the radicals R_5 to R_8 and R_{11} to
20 R_{14} denote phenyl, p-chlorophenyl, p-toluyll or naphthyl radicals or fluorine atoms, or a mixture of these compounds.

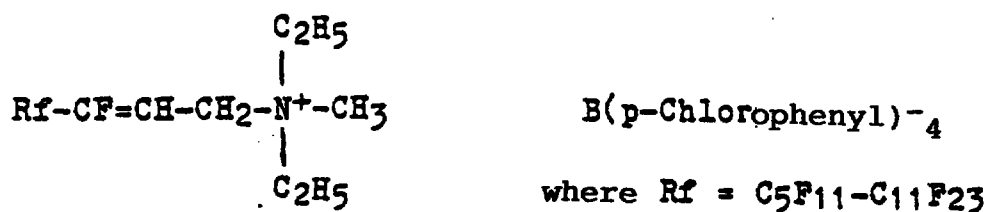
3. A compound of the formula (I) as claimed in claim 1, in which at least one of the radicals R_1 to R_4 denotes
25 the group $-CH_2-CH=CF-R_f$ ($R_f = C_5F_{11}-C_{11}F_{23}$), the group $-CH_2-CH=CF-C_nF_{2n+1}$, where $n = 5, 7$ or 9 , or the group $-CH_2-CH=CF-C_7F_{15}$, and not more than three of the radicals R_1 to R_4 independently of one another denote a methyl, ethyl, butyl or hydroxyethyl group, or a compound of the
30 formula (II) mentioned in claim 1, in which Q, together with the constituent $\overset{(+)}{-N=C-}$, forms a pyridine, pyrazine or quinoline ring system, R_9 denotes a $C_8F_{17}-CH_2-CH_2-$ group, R_{10} denotes a hydrogen atom and the radicals R_5 to R_8 and
35 R_{11} to R_{14} denote phenyl, p-chlorophenyl, p-toluyll or naphthyl radicals or fluorine atoms, or a mixture of these compounds.



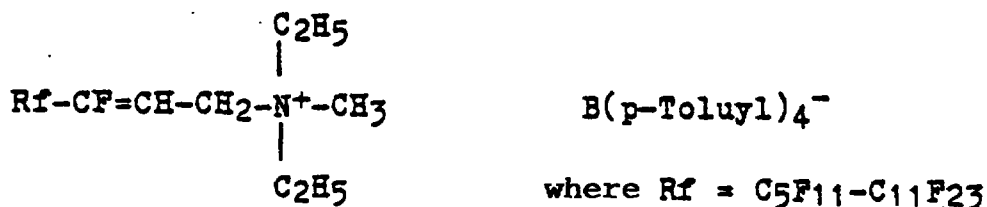
4. A compound or mixture of compounds of the formula



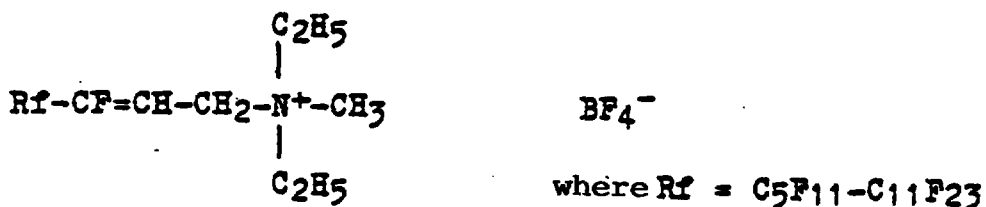
5. A compound or mixture of compounds of the formula



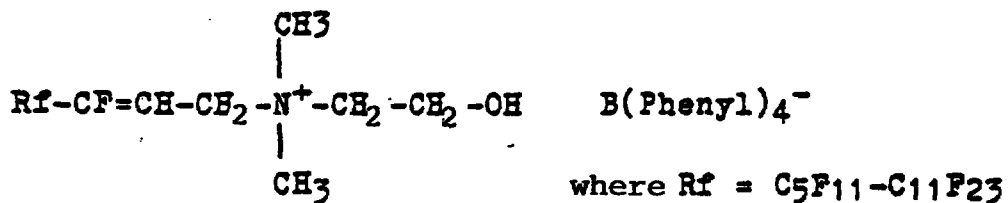
6. A compound or mixture of compounds of the formula



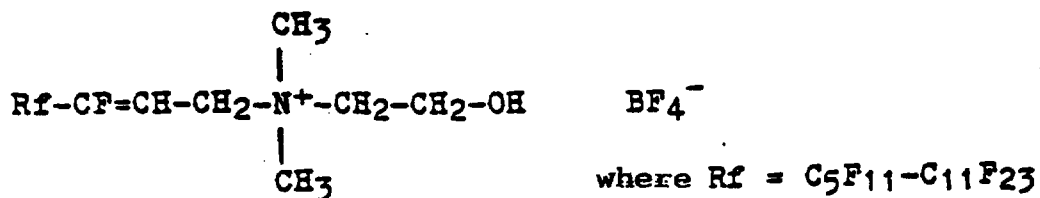
7. A compound or mixture of compounds of the formula



- 5 8. A compound or mixture of compounds of the formula



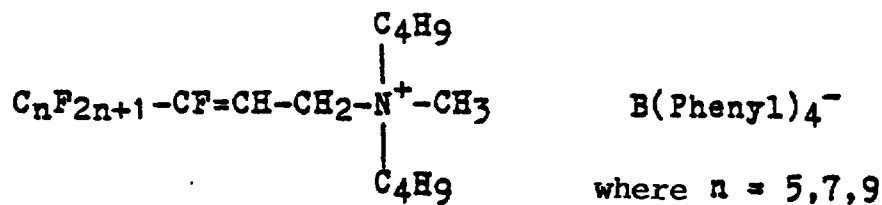
9. A compound or mixture of compounds of the formula



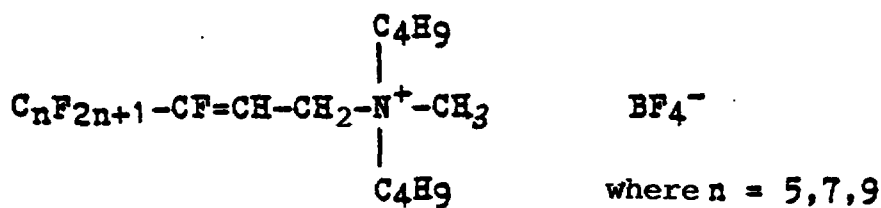


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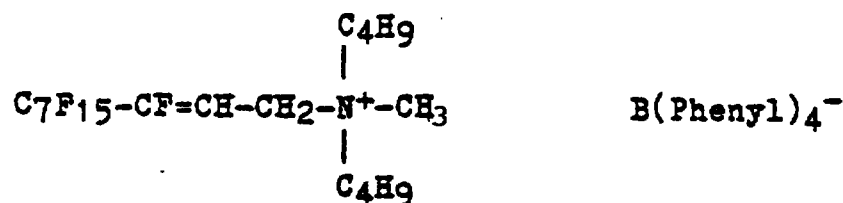
10. A compound or mixture of compounds of the formula



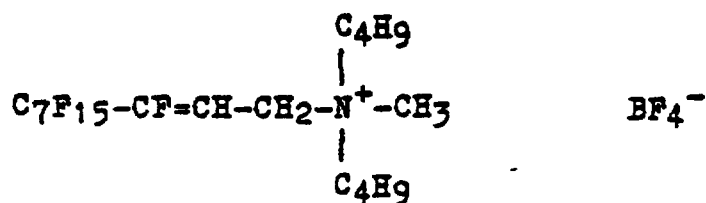
11. A compound or mixture of compounds of the formula



12. The compound of the formula



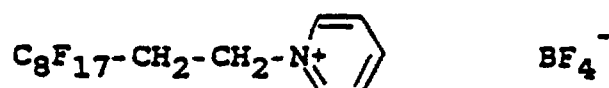
13. The compound of the formula



- 5 14. The compound of the formula

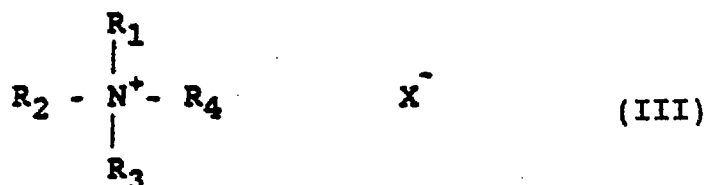


15. The compound of the formula

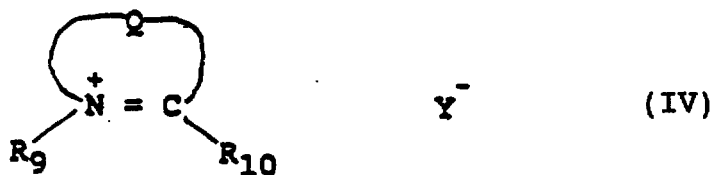




16. A process for the preparation of an ammonium compound or a mixture of ammonium compounds of the formula (I) as claimed in claim 1 or of an iminium compound or a mixture of iminium compounds of the formula (II) as claimed in claim 1, which comprises reacting an ammonium compound or a mixture of ammonium compounds of the formula (III)



- in which at least one of the radicals R_1 to R_4 denotes a straight-chain fluorine-containing unsaturated and/or saturated alkyl radical having 4 to 30 carbon atoms and not more than three of the radicals R_1 to R_4 independently of one another denote hydrogen atoms or straight-chain or branched alkyl or hydroxyalkyl radicals having 1 to 30 carbon atoms, and X^- denotes a halogen anion or a methylsulfate anion, or an iminium compound or a mixture of iminium compounds of the formula (IV) mentioned in claim 1



- in which Q, together with the constituent $\text{N}^+=\text{C}$, forms a mono- or polynuclear ring system having 4 to 17 carbon atoms, which can additionally be interrupted by 1 to 4 hetero atoms and contain 2 to 9 double bonds, and which can be substituted in any desired position by fluorine, chlorine, bromine or iodine atoms or an alkyl($\text{C}_1\text{-C}_6$), alkoxy($\text{C}_1\text{-C}_6$), nitro or amino group, R_9 denotes a fluorine-containing alkyl($\text{C}_1\text{-C}_{30}$) radical, R_{10} denotes a hydrogen, fluorine, chlorine, bromine or iodine atom or an alkyl($\text{C}_1\text{-C}_6$), alkoxy($\text{C}_1\text{-C}_6$), nitro or amino group and Y^- denotes a halogen anion or a methylsulfate anion, with a



borate salt in water or mixtures of water and organic solvent at temperatures of about 20°C to about 90°C.

17. The process as claimed in claim 16, wherein X⁻ in the formula (III) mentioned therein and Y⁻ in the formula
5 (IV) mentioned therein denote a chlorine, bromine or iodine anion.

18. The process as claimed in at least one of claims 16 and 17, wherein the reaction is carried out in a mixture of water and isopropanol, isobutanol or methyl isobutyl
10 ketone.

19. The process as claimed in at least one of claims 16 to 18, wherein the reaction is carried out with sodium tetraphenylborate, sodium tetra-p-chlorophenylborate, sodium tetra-p-toluyllborate or sodium tetrafluoroborate
15 as the borate salt.