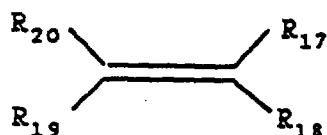
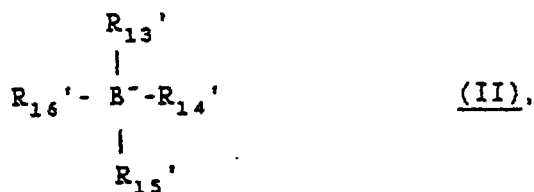
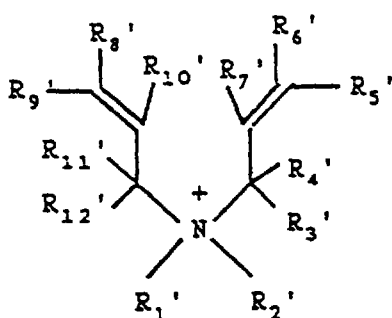
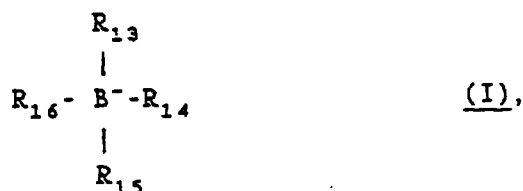
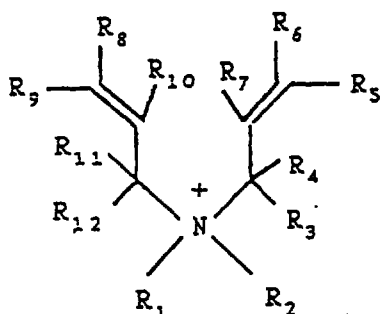


The present invention relates to polymeric ammonium borates based on homopolymeric or copolymeric poly-(diallylammonium) derivatives and copolymers of poly(diallylammonium) derivatives with selected vinyl compounds. The present invention specifically relates to novel polymeric ammonium borates having a molecular weight of 5000 to 500,000, are based on poly(diallylammonium) derivatives or copolymers thereof, having molar monomer ratios (I):(II) and (I):(III) and (II):(III) of 0.5:0.5 to 0.95:0.05 in the copolymer and are prepared by homopolymerization of monomers of the formulae (I) or (II) and by copolymerization of mixtures of two monomers of the formulae (I) to (III), followed, if desired, by anion exchange



(III),

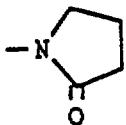
in which the radicals R_1 to R_{16} and R_1' to R_{16}' , independently of one another, are each a hydrogen atom, halogen atom, a hydroxyl radical, a primary, secondary or tertiary amino radical, a carboxyl or carboxylic ester radical, a sulfo or sulfonic ester radical, a cyano or

nitro radical or are each a radical based on a hydrocarbon which may be interrupted by heteroatoms, and the radicals R_{17} to R_{20} , independently of one another, are each a hydrogen atom, chlorine atom, bromine atom, a hydroxyl radical, a primary, secondary or tertiary amino radical, a carboxyl or carboxylic ester radical, a sulfo or sulfonic ester radical, a cyano or nitro radical or are each a radical based on a hydrocarbon which may be interrupted by heteroatoms, in which R_1 and R_2 or R_1' and R_2' , independently of one another, are hydrogen atoms, straight-chain or branched, saturated or unsaturated alkyl(C_1 - C_{18}) or alkoxy(C_1 - C_{18}) radicals, polyoxyalkylene radicals, preferably polyoxyethylene and polyoxypropylene radicals, of the formula $-(\text{alkylene}(C_1-C_5)-O)_n-R$, in which R is a hydrogen atom, an alkyl(C_1 - C_4) radical or an acyl radical, such as, for example, an acetyl, benzoyl or naphthoyl radical, and n is a number from 1 to 10, aryl or heteroaryl radicals, such as, for example, phenyl, naphthyl or pyridyl radicals, aralkyl radicals, such as, for example, tolyl radicals, aralkoxy radicals, such as, for example, methoxyphenyl radicals, alkaryl radicals, such as, for example, benzyl radicals, or cycloalkyl radicals, such as, for example, cyclopentyl or cyclohexyl radicals, and R_1 and R_2 or R_1' and R_2' can also form a saturated or unsaturated, aromatic or non-aromatic 5- to 7-membered ring system, such as, for example, a pyridinium ring system, which may contain further heteroatoms, preferably nitrogen and/or oxygen and/or sulfur atoms, such as, for example, a morpholinium ring system, and may be substituted and/or modified by fusing or bridging to give further ring systems, such as, for example, a quinolinium ring system, in which the radicals R_1 and R_2 or R_1' and R_2' may contain one or more heteroatoms, such as, for example, nitrogen and/or oxygen and/or sulfur and/or phosphorus atoms and may be substituted by halogen atoms, hydroxyl, carboxyl, sulfo, cyano, mercapto radicals, carboxamide radicals, such as, for example, $-NH-C(O)-\text{alkyl}(C_1-C_4)$, sulfonamide radicals, such as, for example, $-NH-SO_2-\text{alkyl}(C_1-C_4)$, urethane radicals, such as,

for example, $\text{-NH-C(O)O-alkyl(C}_1\text{-C}_4\text{)}$, keto radicals, such as, for example, $\text{-C(O)-alkyl(C}_1\text{-C}_4\text{)}$, primary, secondary or tertiary amino radicals, such as, for example, $\text{-NH[alkyl(C}_1\text{-C}_4\text{)]}$, $\text{-N[alkyl(C}_1\text{-C}_4\text{)]}_2$, nitro radicals, ether radicals, such as, for example, $\text{-alkylene(C}_1\text{-C}_4\text{)-O-alkyl(C}_1\text{-C}_4\text{)}$, $\text{alkyl(C}_1\text{-C}_{30}\text{)}$, $\text{alkoxy(C}_1\text{-C}_{30}\text{)}$, aroxy radicals, such as, for example, phenoxy radicals, haloalkyl($\text{C}_1\text{-C}_{30}\text{}$), haloalkoxy($\text{C}_1\text{-C}_{30}\text{}$) or ester radicals, such as, for example, $\text{-C(O)O-alkyl(C}_1\text{-C}_4\text{)}$, and the radicals R_3 to R_{12} or R_3' to R_{12}' , independently of one another, are hydrogen atoms, halogen atoms, straight-chain or branched, saturated or unsaturated alkyl($\text{C}_1\text{-C}_{18}\text{}$) or alkoxy($\text{C}_1\text{-C}_{18}\text{}$) radicals, polyoxyalkylene radicals, preferably polyoxyethylene and polyoxypropylene radicals, of the formula $\text{-(alkylene(C}_1\text{-C}_5\text{)-O)}_n\text{-R}$, in which R is a hydrogen atom, an alkyl($\text{C}_1\text{-C}_4\text{}$) radical or an acyl radical, such as, for example, an acetyl, benzoyl or naphthoyl radical, and n is a number from 1 to 10, aryl or heteroaryl radicals, such as, for example, phenyl, naphthyl or pyridyl radicals, aralkyl radicals, such as, for example, tolyl radicals, aralkoxy radicals, such as, for example, methoxyphenyl radicals, aroxy radicals, such as, for example, phenoxy radicals, alkaryl radicals, such as, for example, benzyl radicals, or cycloalkyl radicals, such as, for example, cyclopentyl or cyclohexyl radicals, and two of the radicals R_3 to R_{12} or R_3' to R_{12}' can also form a saturated or unsaturated, aromatic or non-aromatic 5- to 7-membered ring system, such as, for example, a pyridinium ring system, which may contain further heteroatoms, preferably nitrogen and/or oxygen and/or sulfur atoms, such as, for example, a morpholinium ring system, and may be substituted and/or modified by fusing or bridging to give further ring systems, such as, for example, a quinolinium ring system, in which the radicals R_3 to R_{12} or R_3' to R_{12}' may contain one or more heteroatoms, such as, for example, nitrogen and/or oxygen and/or sulfur and/or phosphorus atoms, and may be substituted by halogen atoms, hydroxyl, carboxyl, sulfo, cyano, mercapto radicals, carboxamide radicals, such as,

for example, $\text{-NH-C(O)-alkyl(C}_1\text{-C}_4\text{)}$, sulfonamide radicals, such as, for example, $\text{-NH-SO}_2\text{-alkyl(C}_1\text{-C}_4\text{)}$, urethane radicals, such as, for example, $\text{-NH-C(O)O-alkyl(C}_1\text{-C}_4\text{)}$, keto radicals, such as, for example, $\text{-C(O)-alkyl(C}_1\text{-C}_4\text{)}$,
5 primary, secondary or tertiary amino radicals, such as, for example, $\text{-NH[alkyl(C}_1\text{-C}_4\text{)]}$, $\text{-N[alkyl(C}_1\text{-C}_4\text{)]}_2$, nitro radicals, ether radicals, such as, for example, $\text{-alkylene(C}_1\text{-C}_4\text{)-O-alkyl(C}_1\text{-C}_4\text{)}$, $\text{alkyl(C}_1\text{-C}_{30}\text{)}$, $\text{alkoxy(C}_1\text{-C}_{30}\text{)}$, aroxy radicals, such as, for example, phenoxy
10 radicals, haloalkyl($\text{C}_1\text{-C}_{30}$), haloalkoxy($\text{C}_1\text{-C}_{30}$) radicals or ester radicals, such as, for example, $\text{-C(O)O-alkyl(C}_1\text{-C}_4\text{)}$, and the radicals R_{13} to R_{16} or R_{13}' to R_{16}' on the borate anion, independently of one another, are aliphatic, cycloaliphatic radicals, aryl or heteroaryl or
15 aralkyl radicals, it being possible for these radicals to be substituted by $\text{alkyl(C}_1\text{-C}_4\text{)}$, $\text{alkoxy(C}_1\text{-C}_4\text{)}$, aryl radicals or halogen atoms, or are fluorine atoms, and the radicals R_{17} to R_{20} , independently of one another, are hydrogen atoms, chlorine atoms, bromine atoms, straight-
20 chain or branched, saturated or unsaturated $\text{alkyl(C}_1\text{-C}_{30}\text{)}$ radicals, polyoxyalkylene radicals, preferably polyoxyethylene and polyoxypropylene radicals, of the formula $\text{(alkylene(C}_1\text{-C}_5\text{)-O)}_n\text{-R}$, in which R is a hydrogen atom, an $\text{alkyl(C}_1\text{-C}_4\text{)}$ radical or an acyl radical, such as, for
25 example, an acetyl, benzoyl or naphthoyl radical, and n is a number from 1 to 10, aryl or heteroaryl radicals, such as, for example, phenyl, naphthyl or pyridyl radicals, aralkyl radicals, such as, for example, tolyl radicals, aralkoxy radicals, such as, for example,
30 methoxyphenyl radicals, alkaryl radicals, such as, for example, benzyl radicals, or cycloalkyl radicals, such as, for example, cyclopentyl or cyclohexyl radicals, carboxyl, sulfo, cyano radicals, carboxamide radicals, such as, for example, $\text{-NH-C(O)-alkyl(C}_1\text{-C}_4\text{)}$, sulfonamide
35 radicals, such as, for example, $\text{-NH-SO}_2\text{-alkyl(C}_1\text{-C}_4\text{)}$, ester radicals, such as, for example, $\text{-CO(O)-alkyl(C}_1\text{-C}_4\text{)}$, carboxylate radicals, such as, for example, $\text{-O-C(O)-alkyl(C}_1\text{-C}_4\text{)}$, keto radicals, such as, for example, $\text{-C(O)-alkyl(C}_1\text{-C}_4\text{)}$, lactam radicals, such as,

for example,



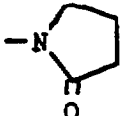
, or ether radicals, such as, for example,

-alkylene(C₁-C₄)-O-alkyl(C₁-C₄), in which the radicals R₁₇ to R₂₀ may contain one or more heteroatoms, such as, for example, nitrogen and/or oxygen and/or sulfur and/or phosphorus atoms, and may be substituted by chlorine or bromine atoms, hydroxyl, carboxyl or sulfo, cyano, mercapto radicals, carboxamide radicals, such as, for example, -NH-C(O)-alkyl(C₁-C₄), sulfonamide radicals, such as, for example, -NH-SO₂-alkyl(C₁-C₄), primary, secondary or tertiary amino radicals, such as, for example, -NH[alkyl(C₁-C₄)], -N[alkyl(C₁-C₄)]₂, or nitro radicals, and in the case of homopolymerization of monomers of the formulae (I) or (II) it being possible for R₁ and R₂ and/or R₁' and R₂' to be identical or different, and in the case of copolymerization of mixtures of two monomers of the formulae (I) to (III) it being possible for not only the radicals R₁ and R₂ and/or R₁' and R₂' but also the borate anions to be identical or different, and to mixtures of these compounds.

The invention relates in particular to polymeric ammonium borates which have a molecular weight of 20,000 to 250,000, are based on poly(diallylammonium) derivatives and copolymers thereof, have molar monomer ratios of (I):(II) and (I):(III) and (II):(III) of 0.5:0.5 to 0.95:0.05 in the copolymer, and are prepared by homopolymerization of monomers of the abovementioned formula (I) or (II) and by copolymerization of mixtures of two monomers of the abovementioned formulae (I) to (III), followed, if desired, by anion exchange, in which R₁ and R₂ or R₁' and R₂', independently of one another, are hydrogen atoms, straight-chain or branched, saturated or unsaturated alkyl(C₁-C₈) or alkoxy(C₁-C₈) radicals, aryl or heteroaryl radicals, such as, for example, phenyl, naphthyl or pyridyl radicals, aralkyl radicals, such as, for example, tolyl radicals, aralkoxy radicals, such as,

for example, methoxyphenyl radicals, alkaryl radicals, such as, for example, benzyl radicals, or cycloalkyl radicals, such as, for example, cyclopentyl or cyclohexyl radicals, it being possible for the radicals R_1 and R_2 or R_1' and R_2' to be substituted by halogen atoms, hydroxyl, carboxyl, sulfo radicals, carboxamide radicals, such as, for example, $-\text{NH}-\text{C}(\text{O})-\text{alkyl}(\text{C}_1-\text{C}_4)$, sulfonamide radicals, such as, for example, $-\text{NH}-\text{SO}_2-\text{alkyl}(\text{C}_1-\text{C}_4)$, keto radicals, such as, for example, $-\text{C}(\text{O})-\text{alkyl}(\text{C}_1-\text{C}_4)$, primary, secondary or tertiary amino radicals, such as, for example, $-\text{NH}[\text{alkyl}(\text{C}_1-\text{C}_4)]$, $-\text{N}[\text{alkyl}(\text{C}_1-\text{C}_4)]_2$, nitro radicals, ether radicals, such as, for example, $-\text{alkylene}(\text{C}_1-\text{C}_4)-\text{O}-\text{alkyl}(\text{C}_1-\text{C}_4)$, alkyl(C_1-C_4), alkoxy(C_1-C_4), aroxy radicals, such as, for example, phenoxy radicals, haloalkyl(C_1-C_4), haloalkoxy(C_1-C_4) radicals or ester radicals, such as, for example, $-\text{C}(\text{O})\text{O}-\text{alkyl}(\text{C}_1-\text{C}_4)$, and the radicals R_3 to R_{12} or R_3' to R_{12}' , independently of one another, are hydrogen atoms, halogen atoms, straight-chain or branched, saturated or unsaturated alkyl(C_1-C_8) or alkoxy(C_1-C_8) radicals, aryl or heteroaryl radicals, such as, for example, phenyl, naphthyl or pyridyl radicals, aralkyl radicals, such as, for example, tolyl radicals, aralkoxy radicals, such as, for example, methoxyphenyl radicals, aroxy radicals, such as, for example, phenoxy radicals, alkaryl radicals, such as, for example, benzyl radicals or cycloalkyl radicals, such as, for example, cyclopentyl or cyclohexyl radicals, it being possible for the radicals R_3 to R_{12} or R_3' to R_{12}' to be substituted by halogen atoms, hydroxyl, carboxyl, sulfo radicals, carboxamide radicals, such as, for example, $-\text{NH}-\text{C}(\text{O})-\text{alkyl}(\text{C}_1-\text{C}_4)$, sulfonamide radicals, such as, for example, $-\text{NH}-\text{SO}_2-\text{alkyl}(\text{C}_1-\text{C}_4)$, keto radicals, such as, for example, $-\text{C}(\text{O})-\text{alkyl}(\text{C}_1-\text{C}_4)$, primary, secondary or tertiary amino radicals, such as, for example, $-\text{NH}[\text{alkyl}(\text{C}_1-\text{C}_4)]$, $-\text{N}[\text{alkyl}(\text{C}_1-\text{C}_4)]_2$, nitro radicals, ether radicals, such as, for example, $-\text{alkylene}(\text{C}_1-\text{C}_4)-\text{O}-\text{alkyl}(\text{C}_1-\text{C}_4)$, alkyl(C_1-C_4), alkoxy(C_1-C_4), aroxy radicals, such as, for example, phenoxy radicals, haloalkyl(C_1-C_4), haloalkoxy(C_1-C_4) radicals or ester radicals, such as,

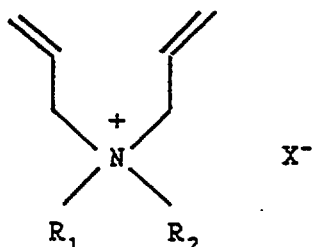
for example, $-C(O)O\text{-alkyl}(C_1\text{-}C_4)$, and the radicals R_{13} to R_{16} or R_{13}' to R_{16}' are phenyl, naphthyl, fluorophenyl, chlorophenyl, methoxyphenyl, biphenyl, pyridyl, tolyl radicals or fluorine atoms, and the radicals R_{17} to R_{20} , independently of one another, are hydrogen atoms, straight-chain or branched, saturated or unsaturated alkyl($C_1\text{-}C_3$) radicals, aryl or heteroaryl radicals, such as, for example, phenyl, naphthyl or pyridyl radicals, aralkyl radicals, such as, for example, tolyl radicals, aralkoxy radicals, such as, for example, methoxyphenyl radicals, alkaryl radicals, such as, for example, benzyl radicals, cycloalkyl radicals, such as, for example, cyclopentyl or cyclohexyl radicals, carboxyl, sulfo, cyano radicals, ester radicals, such as, for example, $-C(O)O\text{-alkyl}(C_1\text{-}C_4)$, carboxylate radicals, such as, for example, $-O\text{-}C(O)\text{-alkyl}(C_1\text{-}C_4)$, carboxamide radicals, such as, for example, $-NH\text{-}C(O)\text{-alkyl}(C_1\text{-}C_4)$, sulfonamide radicals, such as, for example, $-NH\text{-}SO_2\text{-alkyl}(C_1\text{-}C_4)$, keto radicals, such as, for example, $-C(O)\text{-alkyl}(C_1\text{-}C_4)$, lactam radicals, such as, for

example, , or ether radicals, such as, for

example, $\text{-alkylene}(C_1\text{-}C_4)\text{-}O\text{-alkyl}(C_1\text{-}C_4)$, it being possible for the radicals R_{17} to R_{20} to be substituted by chlorine or bromine atoms, hydroxyl, carboxyl, sulfo, cyano, mercapto, carboxamide radicals, such as, for example, $-NH\text{-}C(O)\text{-alkyl}(C_1\text{-}C_4)$, sulfonamide radicals, such as, for example, $-NH\text{-}SO_2\text{-alkyl}(C_1\text{-}C_4)$, primary, secondary or tertiary amino radicals, such as, for example, $-NH[\text{alkyl}(C_1\text{-}C_4)]$, $-N[\text{alkyl}(C_1\text{-}C_4)]_2$, or nitro radicals, and to mixtures of these compounds and mixed crystals containing mixed anions and/or cations.

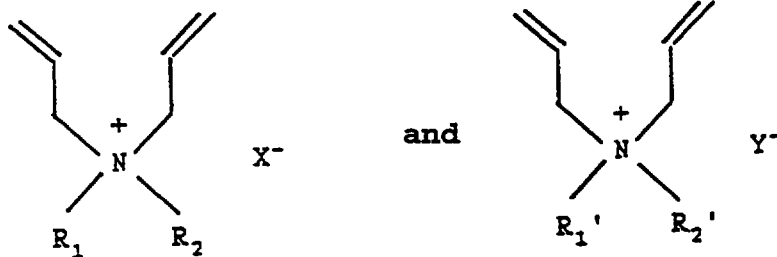
Examples of very particularly suitable compounds are:

- homopolymers of



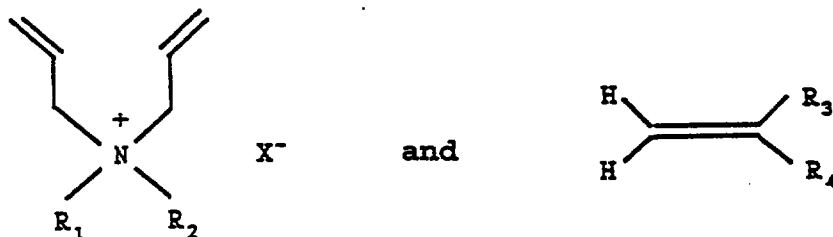
5 where X^- is BF_4^- , $\text{B}(\text{phenyl})_4^-$, R_1 is H, CH_3 , R_2 is CH_3 , C_8H_{17} having a molecular weight of 20,000 to 250,000,

- copolymers of



10 where X^- and Y^- are BF_4^- , $\text{B}(\text{phenyl})_4^-$, R_1 and R_1' are H, CH_3 , R_2 and R_2' are CH_3 , C_8H_{17} , having a molecular weight of 20,000 to 250,000 and a molar monomer ratio in the copolymer of 0.5:0.5 to 0.95:0.05,

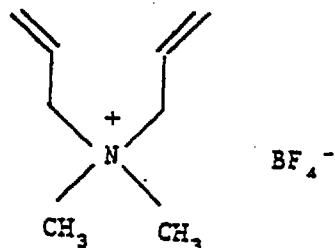
- copolymers of



15 where X^- and Y^- are BF_4^- , $\text{B}(\text{phenyl})_4^-$, R_1 is H, CH_3 , R_2 is CH_3 , C_8H_{17} , R_3 is H, CH_3 , R_4 is COOH , $\text{C}(\text{O})\text{OCH}_3$, $\text{C}(\text{O})\text{OC}_2\text{H}_5$, $\text{C}(\text{O})\text{NH}_2$, $\text{OC}(\text{O})\text{CH}_3$, CN , having a molecular weight of 20,000 to 250,000 and a molar monomer ratio in the copolymer of 0.5:0.5 to 0.95:0.05.

Examples of individual compounds are

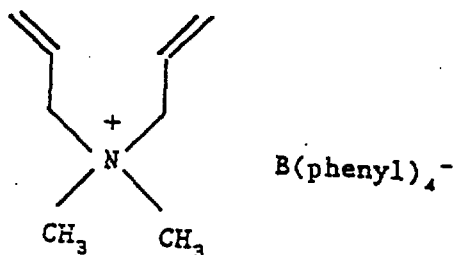
- a homopolymer of



(1)

having a molecular weight of about 100,000,

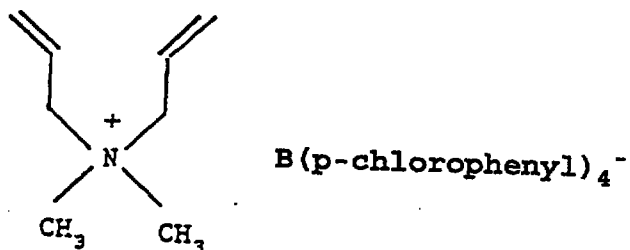
- 5 - a homopolymer of



(2)

having a molecular weight of about 100,000,

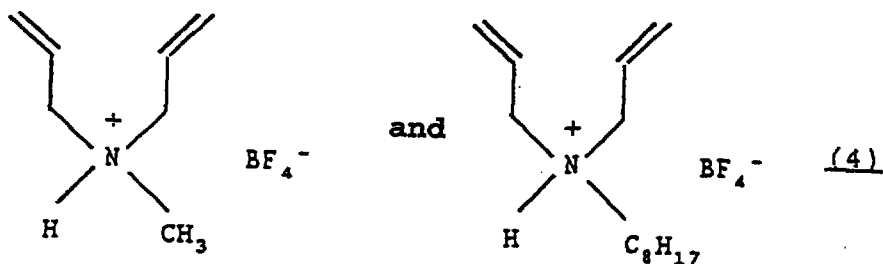
- a homopolymer of



(3)

- 10 - having a molecular weight of about 100,000,

- a copolymer of

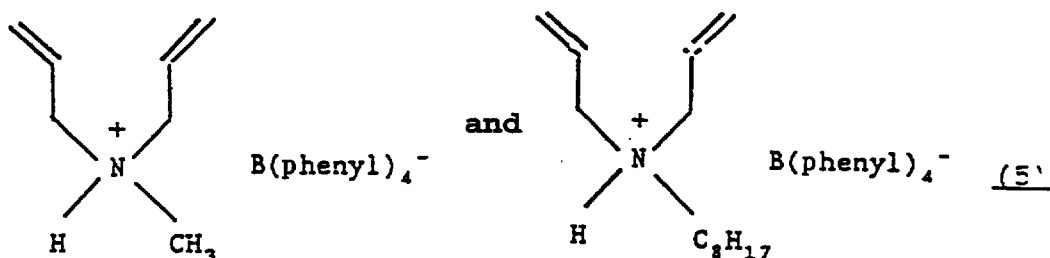


(4)

having a molecular weight of about 100,000 and a

molar monomer ratio in the copolymer of 0.8:0.2,

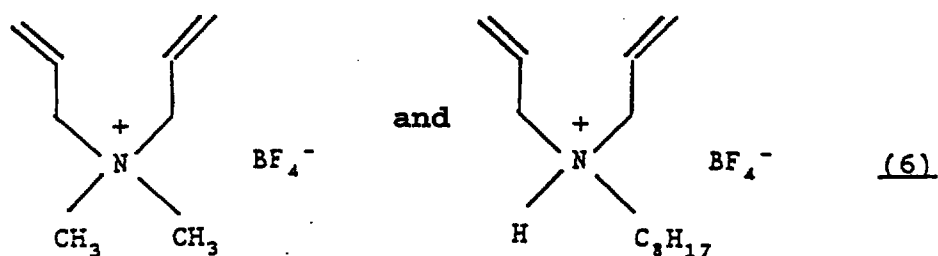
- a copolymer of



having a molecular weight of about 100,000 and a molar monomer ratio in the copolymer of 0.8:0.2,

5

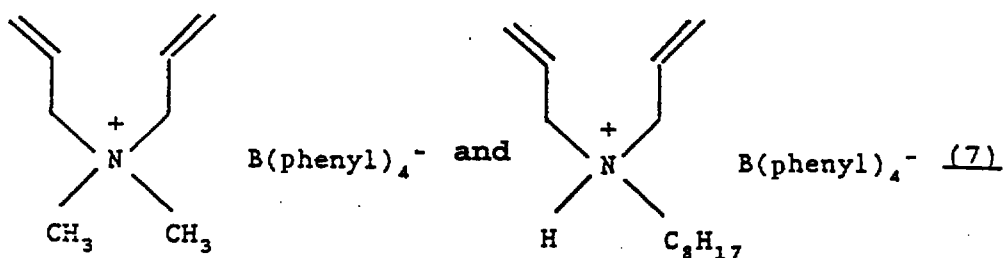
- a copolymer of



having a molecular weight of about 100,000 and a molar monomer ratio in the copolymer of 0.8:0.2,

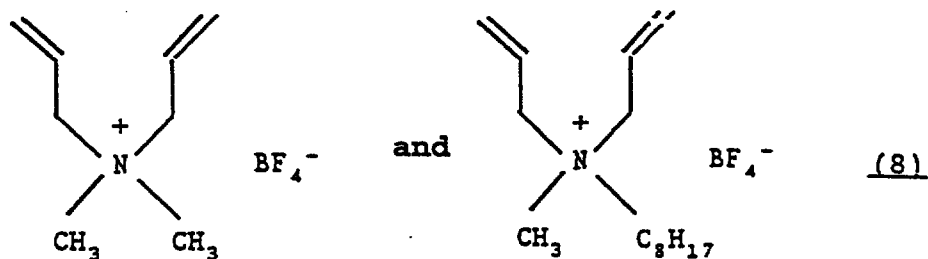
10

- a copolymer of



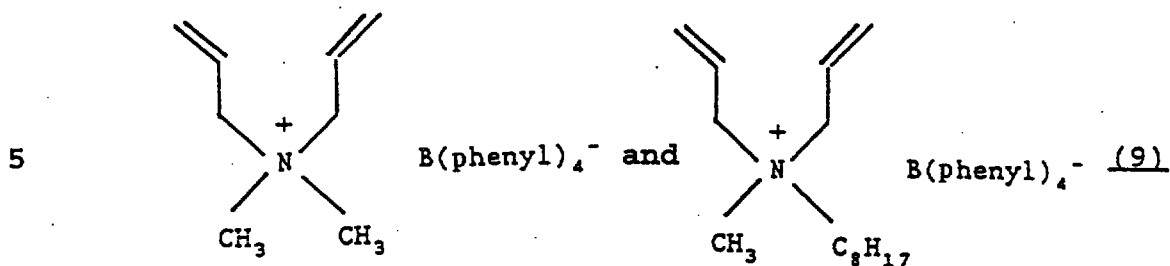
having a molecular weight of about 100,000 and a molar monomer ratio in the copolymer of 0.8:0.2,

- a copolymer of



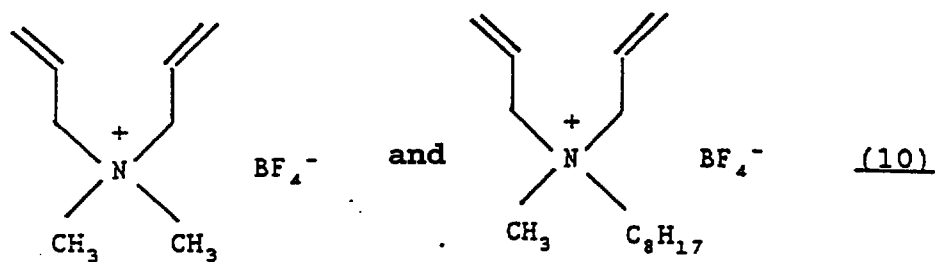
having a molecular weight of about 100,000 and a molar monomer ratio in the copolymer of 0.95:0.05,

a copolymer of



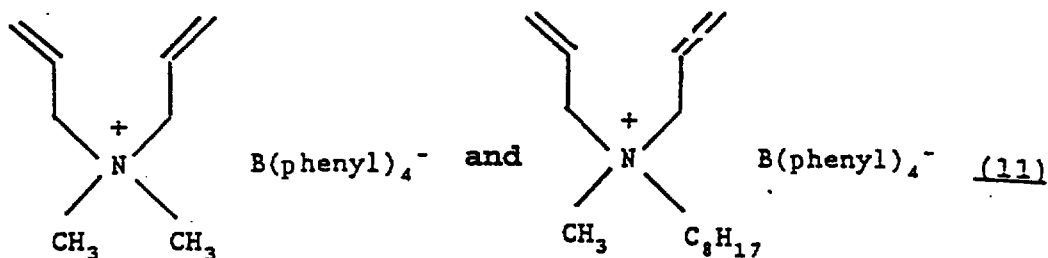
having a molecular weight of about 100,000 and a molar monomer ratio in the copolymer of 0.95:0.05,

a copolymer of



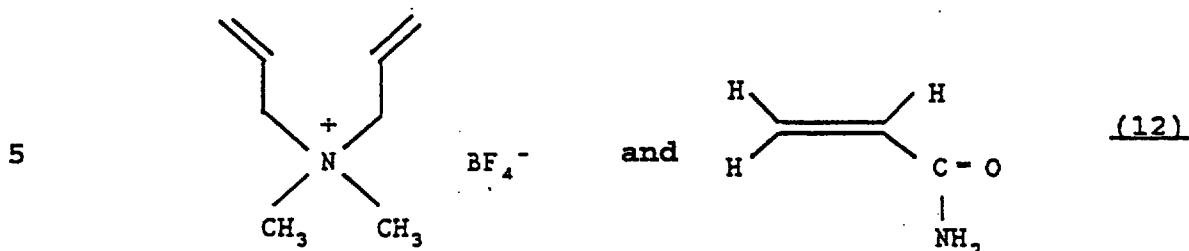
10 having a molecular weight of about 100,000 and a molar monomer ratio in the copolymer of 0.8:0.2,

a copolymer of



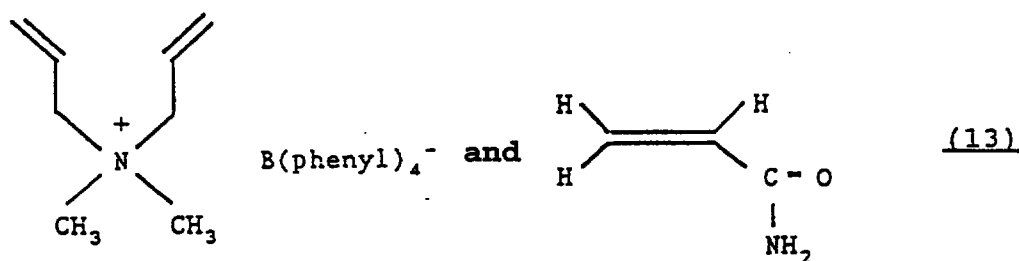
having a molecular weight of about 100,000 and a molar monomer ratio in the copolymer of 0.8:0.2,

- a copolymer of



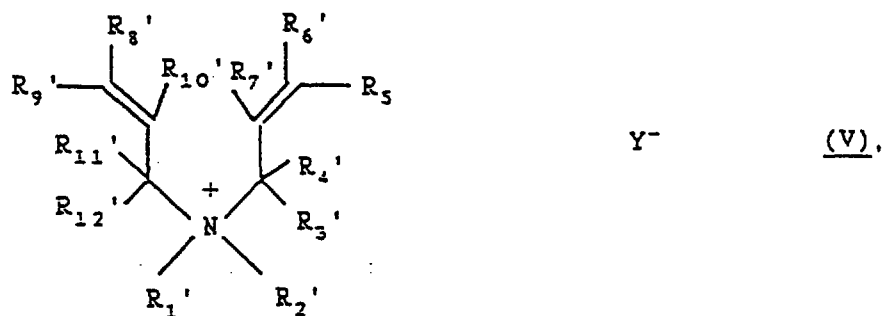
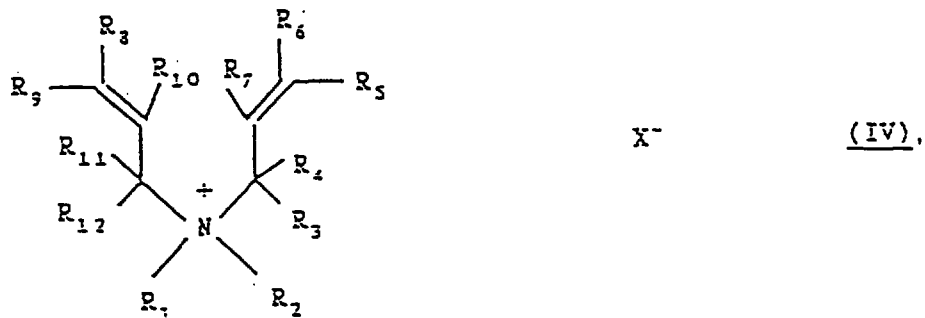
having a molecular weight of about 100,000 and a molar monomer ratio in the copolymer of 0.8:0.2,

- a copolymer of



10 having a molecular weight of about 100,000 and a molar monomer ratio in the copolymer of 0.8:0.2.

15 The compounds of the formulae (I) to (III) and their homo-or copolymers are prepared by homopolymerization of monomers of the formulae (IV) or (V) and by copolymerization of mixtures of two monomers of the formulae (IV) to (VI)



in which the radicals R_1 to R_{12} , R_1' to R_{12}' and R_{17} to R_{20} in the formulae (IV) to (VI) have the meanings given for the formulae (I) to (III) and the anions X^- and Y^- are Cl^- , Br^- , I^- , $CH_3OSO_3^-$ or $C_2H_5OSO_3^-$, and reaction with one or more borate salts in water or mixtures of water and organic solvent, for example a mixture of water and isopropanol, isobutanol or methyl isobutyl ketone, at temperatures of $10^\circ C$ to $90^\circ C$.

- 5 10 15 20
- The preparation of the compounds of the formulae (IV) to (VI) is known and has been described in detail in the literature [e.g. G.B. Butler, R.J. Angelo, J. Am. Chem. Soc. 79 (1957), 3128-31; G.B. Butler in: E.J. Goethals, "Polymeric Amines and Ammonium Salts", Pergamon Press, 1980, 125-42; D.H. Solomon, D.G. Hawthorne, J. Macromol. Sci.-Rev. Macromol. Chem. C15 (1976), 143-64; Houben-Weyl, "Methoden der Organischen Chemie" (Methods of Organic Chemistry), Vol. XIV/1, Thieme-Verlag, Stuttgart, 1961, 561-1182; K. Weissmerl, H.-J. Arpe, "Industrielle Organische Chemie" (Industrial Organic Chemistry), Verlag Chemie, Weinheim, 1988, 230-51; GDR Patent 127729;

European Patent 0103698; US Patent 3288770].

In US-A-4, 452, 957, monomeric quaternary dialkylammonium salts are homopolymerized or copolymerized with olefins. Anions of these polymeric salts which are mentioned are
5 halide, sulfate, borate, phosphate and other conventional inorganic anions.

The compounds of the formulae (IV) and (V) are prepared, for example by reacting allyl halides with N,N-dialkyl-allylamines or by reducing alkyl nitriles, followed by
10 reaction of the amine with allyl halides and quaternization of the diallylamine. Compounds of the formula (VI) are prepared, for example, by an addition reaction of hydrogen halides with ethyne, from ethylene chlorohydrin by reaction with NaCN and alcohols, by esterification of
15 lactic acid followed by thermolysis, by reaction of ethene with acetic acid, by Friedel-Crafts alkylation of aromatics, followed by cracking, by oxidation of propene with ammonia or catalytic hydrolysis of acrylamide. Homopolymers of monomers of the formulae (IV) and (V) and
20 copolymers of mixtures of two monomers of the formulae (IV) to (VI) are prepared, for example, by free-radical homo- or copolymerization under inert gas in polar solvents, such as, for example, water or dimethylformamide, by means of free-radical initiators, such as, for
25 example, t-butyl hydroperoxide or ammonium peroxydisulfate, the preferred monomers used being the halide salts.

Preferred borate salts for reacting according to the process of the invention are sodium tetraphenylborate,
30 sodium tetra-o-fluorophenylborate, sodium tetra-m-fluorophenylborate, sodium tetra-p-fluorophenylborate, sodium tetra-o-chlorophenylborate, sodium tetra-m-chlorophenylborate, sodium tetra-p-chlorophenylborate, sodium tetra-o-tolylborate, sodium tetra-m-tolylborate, sodium tetra-
35 p-tolylborate, sodium tetra-1-naphthylborate, sodium tetra-2-naphthylborate, sodium tetra-o-methoxyphenyl-

borate, sodium tetra-m-methoxyphenylborate, sodium tetra-p-methoxyphenylborate, sodium tetra-o-biphenylborate, sodium tetra-m-biphenylborate, sodium tetra-p-biphenylborate, sodium tetrabenzylborate, sodium tetra-o-pyridylborate, sodium tetra-m-pyridylborate, sodium tetra-p-pyridylborate or sodium tetrafluoroborate.

The various salts, for example of the compounds (1) to (13), are prepared by anion exchange using a borate salt, for example by precipitation from aqueous medium or mixtures of water and organic solvent, such as described in the preparation examples.

The polymeric ammonium borates according to the invention are highly suitable for use as colorless charge-control agents in toners and developers for electrophotographic recording processes and for use as charge-improving agents in powders and coatings for surface coating, in particular in triboelectrically or electrokinetically sprayed powder coatings.

The preparation examples which follow serve to illustrate the invention without limiting it thereto.

PREPARATION EXAMPLES

Preparation Example 1

10 g (0.06 mol) of a homopolymer comprising diallyl-dimethylammonium chloride (molecular weight about 100,000 g/mol) are dissolved in 200 ml of water and 7.5 g (0.07 mol) of sodium tetrafluoroborate dissolved in 100 ml of water are slowly added dropwise at room temperature with stirring. The white precipitate is filtered off with suction, washed chloride-free with water and dried at 100°C in a vacuum drying cabinet.

Yield : 12.2 g (92.4 % of theory) of the compound (1), white powder

Melting point : > 300°C (decomposition)
Elemental analysis : calculated 45.1 % C, 7.5 % H,
6.6 % N, 35.7 % F
found 44.5 % C, 7.9 % H, 6.5 % N,
33.4 % F

5

Preparation Example 2

The procedure of Preparation Example 1 is repeated, except that 24.0 g (0.07 mol) of sodium tetraphenylborate dissolved in 150 ml of water are used instead of sodium tetrafluoroborate.

10

Yield : 27.2 g (98.7 % of theory) of the compound (2), white powder

Melting point : 225°C

Elemental analysis : calculated 86.3 % C, 8.1 % H,
3.1 % N, 2.4 % B

15

found 84.2 % C, 8.1 % H, 3.4 % N,
2.0 % B

Preparation Example 3

10 g (0.06 mol) of a copolymer comprising diallyldimethylammonium chloride and diallylmethyloctylammonium chloride (molecular weight about 100,000 g/mol, molar ratio of the monomer units in the copolymer about 0.8 to 0.2) are dissolved in 400 ml of water, and 7.5 g (0.07 mol) of sodium tetrafluoroborate dissolved in 100 ml of water are slowly added dropwise with stirring at room temperature. The white precipitate is filtered off with suction, washed chloride-free with water and dried at 100°C in a vacuum drying cabinet.

20

25

Yield : 12.4 g (89.9 % of theory) of the compound (6), white powder

30

Melting point : > 300°C (decomposition)

Elemental analysis : calculated 48.0 % C, 8.0 % H,
6.1 % N, 33.0 % F

35

found 46.9 % C, 8.2 % H, 6.2 % N,
32.7 % F

Preparation Example 4

The procedure of Preparation Example 3 is repeated, except that 24.0 g (0.07 mol) of sodium tetraphenylborate dissolved in 150 ml of water are used instead of sodium tetrafluoroborate.

Yield : 26.7 g (96.3 % of theory) of the compound (7), white powder

Melting point : 205-210°C

Elemental analysis : calculated 86.2 % C, 8.3 % H, 3.0 % N, 2.4 % B
found 85.6 % C, 8.4 % H, 3.3 % N, 2.2 % B

Preparation Example 5

10 g (0.06 mol) of a copolymer comprising diallyl-dimethylammonium chloride and diallylmethyloctylammonium chloride (molecular weight about 100,000 g/mol, molar ratio of the monomer units in the copolymer about 0.95 to 0.05) are dissolved in 400 ml of water, and 7.5 g (0.07 mol) of sodium tetrafluoroborate dissolved in 100 ml of water are slowly added dropwise with stirring at room temperature. The amber - colored precipitate is filtered off with suction, washed chloride-free with water and dried at 100°C in a vacuum drying cabinet.

Yield : 9.5 g (72.0% of theory) of the compound (8), amber-colored powder

Melting point : 270°C (decomposition)

Elemental analysis : calculated 46.0 % C, 7.7 % H, 6.4 % N, 5.0 % B
found 45.5 % C, 8.0 % H, 6.7 % N, 4.3 % B

Preparation Example 6

The procedure of Preparation Example 5 is repeated, except that 24.0 g (0.07 mol) of sodium tetraphenylborate

dissolved in 150 ml of water are used instead of sodium tetrafluoroborate.

Yield : 25.8 g (95.6 % of theory) of the compound (9), white powder

5 Melting point : 240°C

Elemental analysis : calculated 86.3 % C, 8.2 % H, 3.1 % N, 2.4 % B
found 85.7 % C, 8.8 % H, 3.0 % N, 2.2 % B

10

Preparation Example 7

10 g (0.08 mol) of a copolymer comprising diallyldimethylammonium chloride and acrylamide (molecular weight about 100,000 g/mol, molar ratio of the monomer units in the copolymer about 0.8 to 0.2) are dissolved in 400 ml of water, and 9.9 g (0.09 mol) of sodium tetrafluoroborate dissolved in 200 ml of water are slowly added dropwise at room temperature with stirring. The white precipitate is filtered off with suction, washed chloride-free with water and dried at 100°C in a vacuum drying cabinet.

20

Yield : 11.6 g (78.2 % of theory) of the compound (12), white powder

Melting point : > 300°C (decomposition)

Elemental analysis : calculated 45.4 % C, 7.5 % H, 7.6 % N, 4.8 % B

25

found 45.1 % C, 7.7 % H, 7.4 % N, 4.3 % B

Preparation Example 8

The procedure of Preparation Example 2 is repeated, except that 33.6 g (0.07 mol) of sodium tetra-p-chlorophenylborate are used instead of sodium tetraphenylborate.

30

Yield : 26.8 g (74.3 % of theory) of the compound (3), white powder

35

Melting point : 210°C

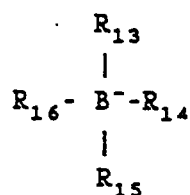
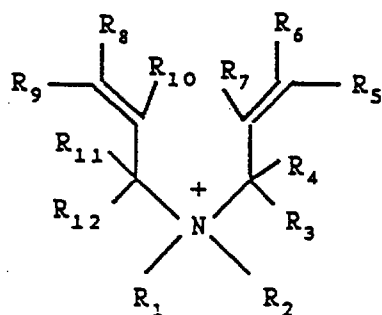
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Elemental analysis : calculated 65.9 % C, 5.5 % H,
24.4 % Cl, 1.9 % B
found 65.2 % C, 5.7 % H,
23.8 % Cl, 1.8 % B



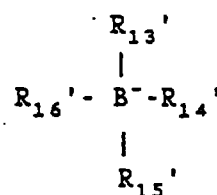
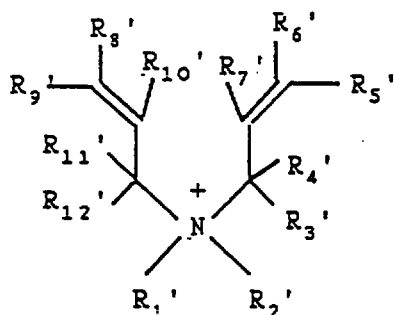
Patent Claims

1. A polymeric ammonium borate having a molecular weight of 5000 to 500,000 and obtained by homopolymerization of monomers of the formulae (I) or (II) and by copolymerization of mixtures of two monomers of the formulae (I) to (III), having molar monomer ratios (I):(II) and (I):(III) and (II):(III) of 0.5:0.5 to 0.95:0.05 in the copolymer, followed, if desired, by anion exchange

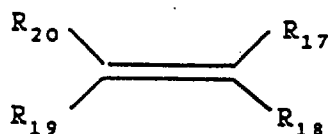


(I).

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(II).



(III).

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in which the radicals R_1 to R_{16} and R_1' to R_{16}' , independently of one another, are each a hydrogen atom, halogen atom, a hydroxyl radical, a primary, secondary or tertiary amino radical, a carboxyl or carboxylic ester radical, a sulfo or sulfonic ester radical, a cyano or nitro radical or are each a radical based on a hydrocarbon which may be interrupted by heteroatoms, and the radicals R_{17} to R_{20} ,



- independently of one another, are each a hydrogen atom, chlorine atom, bromine atom, a hydroxyl radical, a primary, secondary or tertiary amino radical, a carboxyl or carboxylic ester radical, a sulfo or sulfonic ester radical, a cyano or nitro radical or are each a radical based on a hydrocarbon which may be interrupted by heteroatoms, and mixtures of these compounds.
- 5
2. A polymeric ammonium borate as claimed in claim 1, wherein the radicals R_1 and R_2 or R_1' and R_2' , independently of one another, are hydrogen atoms, straight-chain or branched, saturated or unsaturated alkyl(C_1-C_{18}), alkoxy(C_1-C_{18}) radicals, polyoxyalkylene radicals of the formula $-(\text{alkylene}(C_1-C_5)-O)_n-$ R, in which R is a hydrogen atom, an alkyl(C_1-C_4) radical or an acyl radical and n is a number from 1 to 10, aryl or heteroaryl radicals, aralkyl, aralkoxy, alkaryl or cycloalkyl radicals, and R_1 and R_2 or R_1' and R_2' can also form a saturated or unsaturated, aromatic or non-aromatic 5- to 7-membered ring system, which may contain further heteroatoms and may be substituted and/or modified by fusing or bridging to give further ring systems, in which the radicals R_1 and R_2 or R_1' and R_2' may contain one or more heteroatoms, and may be substituted by halogen atoms, hydroxyl, carboxyl, sulfo, cyano, mercapto, carboxamide, sulfonamide, urethane, keto radicals, primary, secondary or tertiary amino radicals, nitro, ether, alkyl(C_1-C_{30}), alkoxy(C_1-C_{30}), aroxy, haloalkyl(C_1-C_{30}), haloalkoxy(C_1-C_{30}) or ester radicals.
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- 15
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- 25
- 30
3. A polymeric ammonium borate as claimed in at least one of claims 1 or 2, wherein the radicals R_3 to R_{12} or R_3' to R_{12}' , independently of one another, are hydrogen atoms, halogen atoms, straight-chain or branched, saturated or unsaturated alkyl(C_1-C_{18}), alkoxy(C_1-C_{18}) radicals, polyoxyalkylene radicals of
- 35



the formula $-(\text{alkylene}(\text{C}_1-\text{C}_5)-\text{O})_n-\text{R}$, in which R is a hydrogen atom, an alkyl(C_1-C_4) radical or an acyl radical and n is a number from 1 to 10, aryl or heteroaryl radicals, aralkyl, aralkoxy, aroxy, alkaryl or cycloalkyl radicals, and two of the radicals R_3 to R_{12} or R_3' to R_{12}' can also form a saturated or unsaturated, aromatic or non-aromatic 5- to 7-membered ring system, which may contain further heteroatoms and may be substituted and/or modified by fusing or bridging to give further ring systems, in which the radicals R_3 and R_{12} or R_3' and R_{12}' may contain one or more heteroatoms, and may be substituted by halogen atoms, hydroxyl, carboxyl, sulfo, cyano, mercapto, carboxamide, sulfonamide, urethane, keto radicals, primary, secondary or tertiary amino radicals, nitro, ether, alkyl(C_1-C_{30}), alkoxy(C_1-C_{30}), aroxy, haloalkyl(C_1-C_{30}), haloalkoxy(C_1-C_{30}) or ester radicals.

4. A polymeric ammonium borate as claimed in at least one of claims 1 to 3, wherein the radicals R_{13} to R_{16} or R_{13}' to R_{16}' on the borate anion, independently of one another, are aliphatic, cycloaliphatic radicals, aryl or heteroaryl radicals or aralkyl radicals, it being possible for these radicals to be substituted by alkyl(C_1-C_4), alkoxy(C_1-C_4), aryl radicals or halogen atoms, or are fluorine atoms.

5. A polymeric ammonium borate as claimed in at least one of claims 1 to 4, wherein the radicals R_{17} to R_{20} , independently of one another, are hydrogen atoms, chlorine atoms, bromine atoms, straight-chain or branched, saturated or unsaturated alkyl(C_1-C_{30}) radicals, polyoxyalkylene radicals of the formula $-(\text{alkylene}(\text{C}_1-\text{C}_5)-\text{O})_n-\text{R}$, in which R is a hydrogen atom, an alkyl(C_1-C_4) radical or an acyl radical and n is a number from 1 to 10, aryl or heteroaryl radicals, aralkyl, aralkoxy, alkaryl or cycloalkyl radicals, carboxyl, sulfo, cyano, carboxamide,

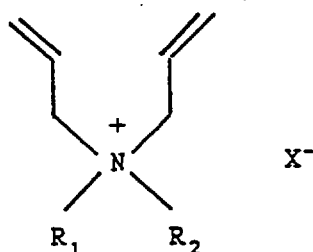


- 5 sulfonamide, ester, carboxylate, keto, lactam or ether radicals, in which the radicals R_{17} to R_{20} may contain one or more heteroatoms, and may be substituted by chlorine or bromine atoms, hydroxyl, carboxyl, sulfo, cyano, mercapto, carboxamide, sulfonamide radicals, primary, secondary or tertiary amino radicals or nitro radicals.
6. A polymeric ammonium borate as claimed in at least one of claims 1 to 5, wherein in the case of homopolymerization of monomers of the formulae (I) or (II) R_1 and R_2 and/or R_1' and R_2' can be identical or different, and in the case of copolymerization of mixtures of two monomers of the formulae (I) to (III) it being possible for not only the radicals R_1 and R_2 and/or R_1' and R_2' but also the borate anions to be identical or different.
7. A polymeric ammonium borate as claimed in at least one of claims 1 to 6, wherein in the formulae (I) to (III) mentioned in claim 1 the radicals R_1 and R_2 or R_1' and R_2' , independently of one another, are hydrogen atoms, alkyl(C_1-C_8), cyclopentyl, cyclohexyl, phenyl, naphthyl, pyridyl, benzyl, tolyl or methoxyphenyl radicals, it being possible for the radicals mentioned to be substituted by halogen atoms, hydroxyl, cyano, mercapto radicals, primary, secondary or tertiary amino radicals or nitro radicals, and the radicals R_3 to R_{12} or R_3' to R_{12}' , independently of one another, are hydrogen atoms, halogen atoms, alkyl(C_1-C_8), cyclopentyl, cyclohexyl, phenyl, naphthyl, pyridyl, benzyl, tolyl or methoxyphenyl radicals, it being possible for the radicals mentioned to be substituted by halogen atoms, hydroxyl, cyano, mercapto radicals, primary, secondary or tertiary amino radicals or nitro radicals, and the radicals R_{13} to R_{16} or R_{13}' to R_{16}' on the borate anion are phenyl, naphthyl, tolyl radicals or fluorine atoms, and the radicals R_{17} to R_{20} ,



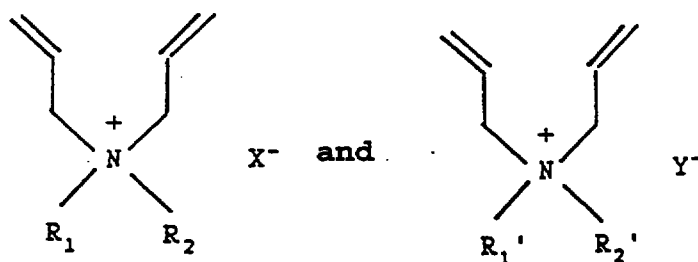
independently of one another, are hydrogen atoms, cyano, alkyl(C₁-C₈), cyclopentyl, cyclohexyl, phenyl, naphthyl, pyridyl, benzyl, tolyl, methoxyphenyl, carboxyl, sulfo, carboxamide, sulfonamide, ester or lactam radicals, it being possible for the radicals mentioned to be substituted by chlorine or bromine atoms, hydroxyl, cyano, mercapto radicals, primary, secondary or tertiary amino radicals or nitro radicals.

- 10 8. A homopolymer of



where X⁻ is BF₄⁻, B(phenyl)₄⁻, R₁ is H, CH₃, R₂ is CH₃, C₈H₁₇, having a molecular weight of 20,000 to 250,000.

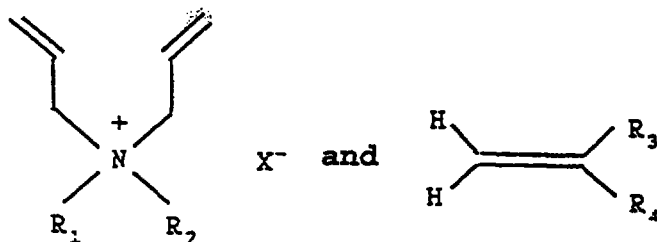
- 15 9. A copolymer of



where X⁻ and Y⁻ are BF₄⁻, B(phenyl)₄⁻, R₁ and R₁' are H, CH₃, R₂ and R₂' are CH₃, C₈H₁₇, having a molecular weight of 20,000 to 250,000 and a molar monomer ratio in the copolymer of 0.5:0.5 to 0.95:0.05.

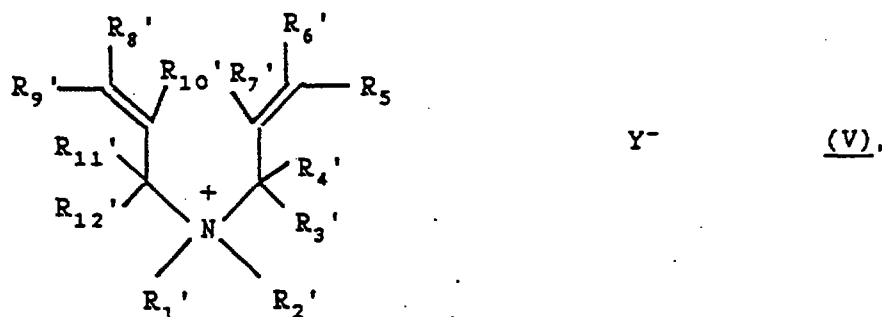
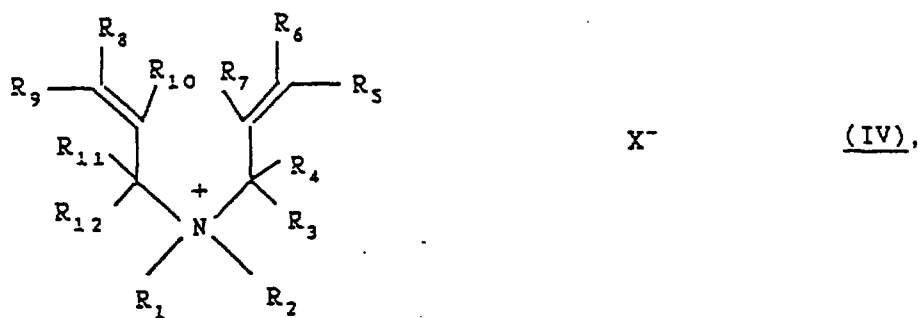


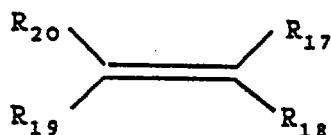
10. A copolymer of



where X^- and Y^- are BF_4^- , $\text{B}(\text{phenyl})_4^-$, R_1 is H, CH_3 , R_2 is CH_3 , C_8H_{17} , R_3 is H, CH_3 , R_4 is COOH , $\text{C}(\text{O})\text{OCH}_3$, $\text{C}(\text{O})\text{OC}_2\text{H}_5$, $\text{C}(\text{O})\text{NH}_2$, $\text{OC}(\text{O})\text{CH}_3$, CN , having a molecular weight of 20,000 to 250,000 and a molar monomer ratio in the copolymer of 0.5:0.5 to 0.95:0.05.

11. A process for the preparation of a polymeric ammonium borate as claimed in claims 1 to 10, which comprises reacting polymer ammonium compounds obtained by homopolymerization of monomers of the formulae (IV) or (V) and by copolymerization of mixtures of two monomers of the formulae (IV) to (VI)





(VI),

in which the radicals R_1 to R_{12} , R_1' to R_{12}' and R_{17} to R_{20} in the formulae (IV) to (VI) have the meanings given for the formulae (I) to (III) in claims 1 to 10 and the anions X^- and Y^- are Cl^- , Br^- , I^- , $CH_3OSO_3^-$ or $C_2H_5OSO_3^-$ with one or more borate salts in water or mixtures of water and organic solvent at temperatures of $10^\circ C$ to $90^\circ C$.

12. The process as claimed in claim 11, wherein the reaction is carried out in a mixture of water and isopropanol, isobutanol or methyl isobutyl ketone.
13. The process as claimed in at least one of claims 11 or 12, wherein the reaction is carried out with sodium tetraphenylborate, sodium tetra-o-fluorophenylborate, sodium tetra-m-fluorophenylborate, sodium tetra-p-fluorophenylborate, sodium tetra-o-chlorophenylborate, sodium tetra-m-chlorophenylborate, sodium tetra-p-chlorophenylborate, sodium tetra-o-tolylborate, sodium tetra-m-tolylborate, sodium tetra-p-tolylborate, sodium tetra-1-naphthylborate, sodium tetra-2-naphthylborate, sodium tetra-o-methoxyphenylborate, sodium tetra-m-methoxyphenylborate, sodium tetra-p-methoxyphenylborate, sodium tetra-o-biphenylborate, sodium tetra-m-biphenylborate, sodium tetra-p-biphenylborate, sodium tetra-benzylborate, sodium tetra-o-pyridylborate, sodium tetra-m-pyridylborate, sodium tetra-p-pyridylborate or sodium tetrafluoroborate.