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POLYMERIC POLY-QUATERNARY AMMONIUM SALTS

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This invention relates to polymeric products and more particularly to new polymeric quaternary ammonium salts.

Polymeric quaternary ammonium salts wherein the nitrogens of the quaternary ammonium salt groups are contained as intralinear substituents in the polymer chain are known in the art. Examples of these compouns are described in U. S. Patents 2,261,002, 2,271,378 and 2,388,614. Such compounds are generally prepared by the reaction between difunctional di-tertiary amines and dihalides. In U. S. Patent No. 2,487,829 of Richards there are disclosed polymeric N-alkyl vinyl pyridinium halides in which the quaternary ammonium salt groups consist of N-alkyl pyridinium type groups, wherein the quaternary nitrogens are those of the pyridine rings, and are attached directly to the main polymer chain. In these pyridinium type quaternary nitrogen compounds three of the valences of the quaternary nitrogens are utilized in the formation of an aromatic ring and the recurring units in the main polymer chain consist predominantly of two carbon hydrocarbon units.

It is an object of this invention to provide new polymeric products. A further object is to provide new polymeric quaternary ammonium salts. A still further object is to provide new polymeric quaternary ammonium salts wherein the quaternary ammonium salt groups are present as extralinear substituents and the nitrogens of said extralinear quarternary ammonium salt groups are bonded, other than to the acid anion salt radicals, solely to aliphatic, cycloaliphatic, saturated heterocyclic and araliphatic substituents, i. e., are singly bonded solely to aliphatic carbon. Other objects will appear hereinafter.

The objects of this invention are accomplished by providing a new class of polymeric polyquaternary ammonium salts which contain recurring quaternary ammonium salt units in which the nitrogen atom is extralinear (i. e., is not an integral part of the main polymer chain) and in which two of the valences of the nitrogen are satisfied by aliphatic cycloaliphatic monovalent hydrocarbon radicals or, monovalent, hydrocarbon radicals which may be joined together in a ring, in which instance a chalcogen of atomic weight less than 33, i. e., oxygen or sulfur, may be part of the ring. A third valence of the nitrogen is satisfied by a monovalent acid anion of an organic or inorganic mono- or polybasic acid of primary acid ionization constant, i. e., K_1, greater than 1.6×10^{-5}, and a fourth valence is satisfied by an aliphatic carbon, which, in turn, is bonded

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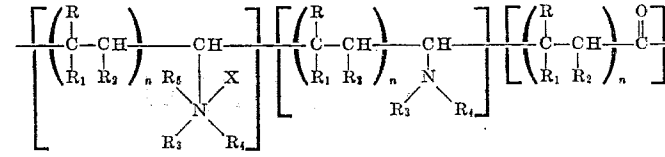
solely to hydrogen and/or hydrocarbon radicals—the above-described two units filling the third and fourth valences of the nitrogen together forming an ester. The fifth and remaining valence of the nitrogen is satisfied by a hydrocarbon radical containing at least three contiguous carbon atoms, at least two of which are an integral part of the main polymer chain. These polymeric poly-quaternary ammonium salts can contain carbonyl carbon in the remaining hydrocarbon radicals containing at least three contiguous carbon atoms at least two of which are an integral part of the main polymer chain—said hydrocarbon radicals joining the above-described quaternary ammonium salt units.

Examples of cycloaliphatic monovalent, hydrocarbon radicals are cyclohexyl, methylcyclohexyl, and the like.

This new class of polymeric poly-quarternary ammonium salts can be obtained by hydrogenating a polymeric ketone in the presence of at least one saturated aliphatic, cycloaliphatic, or heterocyclic secondary monoamine (in the case of the saturated heterocyclic secondary monoamines, the heteroatoms in the cycle, if any, other than the amino nitrogen being chalcogens of atomic weight less than 33) until at least 25% of the carbonyl groups have been converted to extralinear tertiary amine groups and then reacting the resulting polymeric poly-tertiary polyamine with at least one ester until at least 10% of the tertiary amine groups have been quaternized. There can be employed to quaternize the polymeric polytertiary polyamines any ester of an organic or inorganic mono- or polybasic acid of K_1 greater than 1.6×10^{-5} with an alcohol having an alcoholic hydroxyl group bonded directly to an aliphatic carbon which carries, in addition, solely hydrogen and/or hydrocarbon, preferably aliphatically saturated, substituents, said alcohol containing a total of from 1 to 18 carbons.

The intermediate polymeric poly-tertiary polyamines contain recurring structural units in which the nitrogen atom is extralinear and in which two of the valences of the nitrogen are satisfied by monovalent, aliphatic or cycloaliphatic, hydrocarbon radicals which may be joined together in a ring, in which instance a chalcogen of atomic weight less than 33 may be part of said ring, and the remaining valence of the nitrogen is satisfied by a hydrocarbon radical containing at least three contiguous carbon atoms at least two of which are an integral part

of the main polymer chain. These polytertiary polyamines can also contain carbonyl carbon



either as an integral unit of the main polymer chain or extralinearly bonded directly thereto. The preparation of these intermediate polymeric poly-tertiary polyamines is more fully disclosed in U. S. Patents 2,063,158 and 2,495,255.

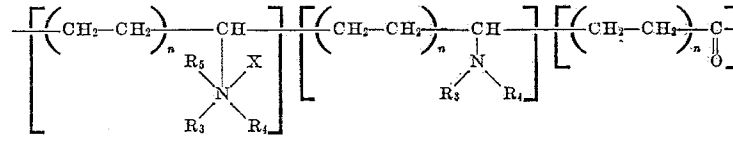
The preferred polymeric quaternary ammonium salts of this invention contain recurring quaternary ammonium salt units in which the nitrogen atom is extralinear and in which two of the valences of the nitrogen are satisfied by monovalent aliphatic or cycloaliphatic hydrocarbon radicals which may be joined together in a ring in which instance a chalcogen of atomic weight less than 33, i. e., oxygen or sulfur may be part of the ring; the third and fourth valences of the nitrogen are satisfied by a monovalent acid anion of an organic or inorganic mono- or polybasic acid of K_1 greater than 1.6×10^{-5} and an aliphatic carbon carrying solely hydrogen and/or hydrocarbon radicals, preferably aliphatically saturated, singly bonded directly thereto—said latter two units, satisfying the third and fourth valences of the nitrogen, together forming an ester of an alcohol and an organic or inorganic acid; and the fifth and remaining valence of the nitrogen is satisfied by an aliphatic hydrocarbon radical containing three contiguous carbon atoms, all of which are a part of the main polymer chain and carrying on the two contiguous carbon atoms in said chain bonded directly to the carbon filling the fifth valence of the nitrogen, hydrogen or short chain hydrocarbon substituents totalling no more than two carbons. These preferred polymeric quaternary ammonium salts can also contain carbonyl carbon in the chain of contiguous carbon atoms comprising the main carbon chain, i. e., there may be carbonyl carbons in the main carbon chain joining the above-described quaternary ammonium salt units.

These preferred polymeric quaternary ammonium salts can be prepared by quaternizing with an ester of an organic or inorganic mono- or polybasic acid of K_1 greater than 1.6×10^{-5} and an alcohol, preferably a monoalcohol, having alcoholic hydroxyl bonded directly to aliphatic carbon which carries, in addition, solely hydrogen and/or hydrocarbon radicals, preferably aliphatically saturated, at least 10% of the extralinear tertiary amine groups in a polymeric polytertiary polyamine which in turn is prepared by reductively aminating with hydrogen and an aliphatic or cycloaliphatic secondary amine at least 25% and preferably 50% of the carbonyl groups in a polymeric polyketone, said polyketone being the polymer of a monoolefin containing from 2 to 4 carbon atoms with carbon monoxide in which the mole ratio of monoolefin to carbon monoxide is from 1:1 to 150:1.

Thus, the preferred polymeric quaternary ammonium salts of this invention will have recurring structural groups of the following formula:

wherein R, R_1, and R_2 are hydrogen or lower alkyl radicals of from 1 to 2 carbon atoms and the total number of carbon atoms, if any, contained in R, R_1 and R_2 taken together cannot exceed 2, i. e., is less than 3, i. e., ranges from 0 to 2; R_3 and R_4 are aliphatic or cycloaliphatic monovalent hydrocarbon radicals of from 1 to 18 carbons each which may be alike or different and may be joined together in a ring, preferably of 5 to 6 ring members, in which instance there may be a chalcogen of atomic weight less than 33 present in the ring structure; R_5 and X together form an organic ester of an alcohol and an organic or inorganic acid used in the quaternization reaction, X being used to indicate the acid portion of the ester, being an acid anion of an organic or inorganic acid of K_1 greater than 1.6×10^{-5}—said acid being mono- or polybasic—but X being attached to the nitrogen by a single bond only, and R_5, the alcohol portion of the ester being singly bonded through aliphatic carbon to the nitrogen and carrying on said aliphatic carbon solely hydrogen and/or hydrocarbon radicals, preferably aliphatically saturated, and containing from 1 to 18 carbons including said aliphatic carbon; and n is a number from 1 to 150 and preferably from 1.5 to 10. In these preferred polymeric poly-quaternary ammonium salts at least 25% and preferably 50% of the recurring structural groups will contain nitrogen atoms of which nitrogen-containing groups at least 10% will contain quaternary ammonium nitrogen atoms. Thus, at least 10% of the nitrogen containing groups will be quaternized.

To further illustrate more specifically the new polymeric poly-quaternary ammonium salts of this invention, the new polymeric poly-quaternary ammonium salts derived from the quaternization of the poly-tertiary polyamines obtained by the reductive amination with an aliphatic, cycloaliphatic, or saturated heterocyclic secondary monoamine of ethylene/carbon monoxide copolymers will contain recurring structural units of the following formula:



where R_3, R_4, R_5, X, and n are defined as aforesaid and at least 25% of the recurring groups contain nitrogen atoms, of which nitrogen-containing groups at least 10% contain quaternary ammonium nitrogen atoms.

The following general description illustrates the preferred manner of preparing the polymeric quaternary ammonium salts of this invention. A slight excess of the ester over the amount theoretically required for the desired degree of conversion of the tertiary amine groups to quaternary salt groups is added to a solution of the poly-tertiary amine in a suitable solvent; for example, liquid hydrocarbons or liquid hydrocarbon/alcohol mixtures such as benzene or a mixture of xylene and isopropyl alcohol. The

resulting solution is allowed to stand at room temperature when the more reactive esters for quaternization are used, such as for instance, methyl iodide or methyl cyclohexanesulfonate. The solution may be, and preferably is, heated to the boiling point when less reactive esters, such as octadecyl bromide, are used for the quaternization. Higher temperatures in the range 180 to 200° C. can also be used in which case it is, of course, necessary that a closed reactor be used to prevent appreciable loss of the reactants. To prevent appreciable decomposition of the products even while carrying out these reactions under pressure, i. e., in a sealed reactor, it is usually preferable not to heat the reactants above 175° C.

The reaction is allowed to proceed for varying amounts of time ranging from 0.5 to 100 hours depending upon the temperature and the reactivity of the ester being used in the quaternization. The polymeric quaternary ammonium salts thus formed generally separate from the solution in the form of powdery solids or as tacky resins. If the product cannot be isolated by filtration, the solvents and excess ester can be removed by distillation under reduced pressure.

The following examples, in which the parts given are by weight, are submitted to further illustrate but not to limit the products of this invention:

Example I

Fifteen (15) parts of methyl iodide are added to a solution of 15 parts of a poly-tertiary amine of neutral equivalent (N. E.) 276 in 135 parts of benzene. The polytertiary amine used had been previously prepared by the reductive amination with dimethylamine of an ethylene/carbon monoxide polyketone of molecular weight 1180 containing ethylene and carbon monoxide in a 3.7:1 combined mole ratio. The solution sets to a solid gel in 45 minutes and is allowed to stand overnight. At the end of this time the granular product, which separates from the reaction mixture, is removed by suction filtration and then dried. There is thus obtained from the parent ethylene/carbon monoxide polyketone 15 parts (68% conversion based on the intermediate poly-tertiary amine) of the polymethylene trimethyl quaternary ammonium iodide as a cream-colored solid, which is readily soluble in water and exhibits positive bactericidal action against *B. typhosa* and *Staphylococcus aureus*.

The starting poly-tertiary polyamine, assuming that all the carbonyl groups in the original polyketone are converted to extralinear tertiary amine groups with dimethylamine, should contain 8.9% nitrogen. Analytical determinations show the starting polyamine to contain 5.88% nitrogen, which figure indicates the conversion of 66% of the carbonyl groups in the parent polyketone to tertiary amine groups, assuming that all the nitrogen present in the poly-tertiary amine is, in fact, resident in tertiary amine groups. On this basis, the conversion of all the tertiary amine groups present in the starting polymeric poly-tertiary polyamine to quaternary ammonium iodide salt groups with methyl iodide would require the final polymeric quaternary ammonium iodide salt to contain 34.8% iodine. Analytical results show the polymethylene trimethyl quaternary ammonium iodide product to contain 33.1% iodine, thus, indicating on this basis the conversion of 95% of the tertiary amine groups to quaternary ammonium iodide salt groups. Thus, the final product contains, using the above assumptions, 34% of the original carbonyl groups of the starting polyketone, 5% of the tertiary amine groups (i. e., 5% of 66% or 3.3% of the original carbonyl groups in the parent polyketone as extralinear tertiary amine groups carrying two methyl substituents directly bonded to the nitrogen) and 95% of the tertiary amine groups as quaternary ammonium iodide groups (i. e., 95% of 66% or 62.7% of the original carbonyl groups of the parent polyketone as extralinear quaternary ammonium iodide groups carrying three methyl radicals and an iodide radical directly bonded to the extralinear nitrogen).

Example II

Forty (40) parts of methyl iodide are added to a solution of 100 parts of a poly-tertiary amine of N. E. 607 in 450 parts of benzene. The poly-tertiary amine used had been previously prepared by the reductive amination with dimethylamine of an ethylene/carbon monoxide polyketone of molecular weight 1650 containing ethylene and carbon monoxide in a 10.9:1 combined mole ratio. The solution is allowed to stand overnight at room temperature and the benzene solvent and unreacted methyl iodide removed by distillation under reduced pressure. There is thus obtained from the parent ethylene/carbon monoxide polyketone 90 parts (73% conversion based on the intermediate poly-tertiary amine) of the poly-methylene trimethyl quaternary ammonium iodide as an amber-colored, stiff resin readily soluble in water.

The starting poly-tertiary polyamine, assuming that all the carbonyl groups in the original polyketone are converted to extralinear tertiary amine groups with dimethylamine, should contain 3.84% nitrogen. Analytical determinations show the starting polyamine to contain 2.41% nitrogen, which figure indicates the conversion of 63% of the carbonyl groups in the parent polyketone to tertiary amine groups, assuming that all the nitrogen present in the poly-tertiary amine is in fact resident in tertiary amine groups. On this basis, the conversion of all the tertiary amine groups present in the starting polymeric poly-tertiary polyamine to quaternary ammonium iodide salt groups with methyl iodide would require the final polymeric quaternary ammonium iodide salt to contain 18.1% iodine. Analytical results show the polymethylene trimethyl quarternary ammonium iodide product to contain 15.2% iodine, thus, indicating on this basis the conversion of 84% of the tertiary amine groups to quaternary ammonium iodide salt groups. Thus, the final product contains, using the above assumptions, 37% of the original carbonyl groups of the starting polyketone, 16% of the tertiary amine groups (i. e., 16% of 63% or 10.1% of the original carbonyl groups in the parent polyketone as extralinear tertiary amine groups carrying two methyl substituents directly bonded to the nitrogen) and 84% of the tertiary amine groups as quaternary ammonium iodide groups (i. e., 84% of 63% or 52.9% of the original carbonyl groups of the parent polyketone as extralinear quaternary ammonium iodide groups carrying three methyl radicals and an iodide radical directly bonded to the extralinear nitrogen).

Example III

Thirty-four (34) parts of methyl iodide are added to a solution of 34 parts of a poly-tertiary amine of N. E. 327 in 180 parts of benzene. The poly-tertiary amine used has been previously pre-

pared by the reductive amination with dimethylamine of an ethylene/carbon monoxide polyketone of molecular weight 1040 containing ethylene and carbon monoxide in a 4.7:1 combined mole ratio. The product is isolated as described in Example II. There is thus obtained from the parent ethylene/carbon monoxide polyketone about 30 parts (61% conversion based on the intermediate poly-tertiary amine) of the polymethylene trimethyl quaternary ammonium iodide as an amber-colored, brittle resin.

The starting poly-tertiary polyamine, assuming that all the carbonyl groups in the original polyketone are converted to extralinear tertiary amine groups with dimethylamine, should contain 7.5% nitrogen. Analytical determinations show the starting polyamine to contain 4.9% nitrogen, which figure indicates the conversion of 65% of the carbonyl groups in the parent polyketone to tertiary amine groups, assuming that all the nitrogen present in the poly-tertiary amine is, in fact, resident in tertiary amine groups. On this basis, the conversion of all the tertiary amine groups present in the starting polymeric poly-tertiary polyamine to quaternary ammonium iodide salt groups with methyl iodide would require the final polymeric quaternary ammonium iodide salt to contain 30.7% iodine. Analytical results show the polymethylene trimethyl quaternary ammonium iodide product to contain 19.4% iodine, thus, indicating on this basis the conversion of 63% of the tertiary amine groups to quaternary ammonium iodide salt groups. Thus, the final product contains, using the above assumptions, 35% of the original carbonyl groups of the starting polyketone, 37% of the tertiary amine groups (i. e., 37% of 65% or 24.0% of the original carbonyl groups in the parent polyketone as extralinear tertiary amine groups carrying two methyl substituents directly bonded to the nitrogen) and 63% of the tertiary amine groups as quaternary ammonium iodide groups (i. e., 63% to 65% or 41% of the original carbonyl groups of the parent polyketone as extralinear quaternary ammonium iodide groups carrying three methyl radicals and an iodide radical directly bonded to the extralinear nitrogen).

Example IV

Thirteen and two-tenths (13.2) parts of freshly distilled benzyl chloride are added to a solution of 34 parts of the poly-tertiary amine described in Example III in 280 parts of benzene. The solution is allowed to stand overnight and the product isolated as described in Example II. There is thus obtained from the parent ethylene/carbon monoxide polyketone about 30 parts (64% conversion based on the intermediate poly-tertiary amine) of the polymethylene dimethyl-benzyl quaternary ammonium chloride as a straw-colored, hard resin readily soluble in water.

As previously discussed in Example III analytical results on the starting poly-tertiary polyamine show the conversion of 65% of the carbonyl groups in the parent polyketone to tertiary amine groups with dimethylamine, assuming that all the nitrogen present in the poly-tertiary amine is, in fact, resident in tertiary amine groups. On this basis, the conversion of all the tertiary amine groups present in the starting polymeric poly-tertiary polyamine to quaternary ammonium chloride salt groups with benzyl chloride would require the final polymeric quaternary ammonium chloride salt to contain 8.9% chlorine. Analytical results show the polymethylene dimethylbenzyl quaternary ammonium chloride product to contain 6.0% chlorine, thus, indicating on this basis the conversion of 67% of the tertiary amine groups to quaternary ammonium chloride salt groups. Thus, the final product contains, using the above assumptions, 35% of the original carbonyl groups of the starting polyketone, 33% of the tertiary amine groups (i. e., 33% of 65% or 20.4% of the original carbonyl groups in the parent polyketone as extralinear tertiary amine groups carrying two methyl substituents directly bonded to the nitrogen) and 67% of the tertiary amine groups as quaternary ammonium chloride groups (i. e., 67% of 65% or 44.6% of the original carbonyl groups of the parent polyketone as extralinear quaternary ammonium chloride groups carrying two methyl, one benzyl and one chloride radical directly bonded to the extralinear nitrogen).

Example V

Thirty-six (36) parts of methyl iodide are added to a solution of 33 parts of a poly-tertiary amine of N. E. 218 in 225 parts of benzene. The poly-tertiary amine used had been previously prepared by the reductive amination with dimethylamine of an ethylene/carbon monoxide polyketone of molecular weight 1990, containing ethylene and carbon monoxide in a 1.5:1 combined mole ratio. The solution warms spontaneously soon after mixing, and the solid polymeric quaternary ammonium salt begins to separate after a period of 10 minutes. The mixture is allowed to stand at room temperature for about 90 minutes, and the product isolated by suction filtration and then dried. There is thus obtained from the parent ethylene/carbon monoxide polyketone through the intermediate poly-tertiary amine the polymethylene trimethyl quaternary ammonium iodide as a buff-colored, powdery product soluble in water.

The starting poly-tertiary polyamine, assuming that all the carbonyl groups in the original polyketone are converted to extralinear tertiary amine groups with dimethylamine, should contain 13.9% nitrogen. Analytical determinations show the starting polyamine to contain 8.14% nitrogen, which figure indicates the conversion of 59% of the carbonyl groups in the parent polyketone to tertiary amine groups, assuming that all the nitrogen present in the poly-tertiary amine is, in fact, resident in tertiary amine groups. On this basis, the conversion of all the tertiary amine groups present in the starting polymeric poly-tertiary polyamine to quaternary ammonium iodide salt groups with methyl iodide would require the final polymeric quaternary ammonium iodide salt to contain 43.0% iodine. Analytical results show the polymethylene trimethyl quaternary ammonium iodide product to contain 7.8% iodine, thus, indicating on this basis the conversion of 18.0% of the tertiary amine groups to quaternary ammonium iodide salt groups. Thus, the final product contains, using the above assumptions, 41% of the original carbonyl groups of the starting polyketone, 82% of the tertiary amine groups (i. e., 82% of 59% or 48.4% of the original carbonyl groups in the parent polyketone as extralinear tertiary amine groups carrying two methyl substituents directly bonded to the nitrogen) and 18% of the tertiary amine groups as quaternary ammonium iodide groups (i. e., 18% of 59% or 10.6% of the original carbonyl groups of the parent polyketone as extralinear quaternary ammonium iodide groups

carrying three methyl radicals and an iodide radical directly bonded to the extralinear nitrogen).

In this connection, it should be pointed out that the poly-tertiary amines used in preparing the preferred products of this invention, i. e., the poly-tertiary amines obtained by the reductive amination with secondary amines of the monoolefin/carbon monoxide polyketones also contain primary and secondary amine groups. In some instances, the proportions of primary and secondary amine groups are relatively high, but in no instance do they together account for more of the amino nitrogen in the polyamines so prepared than the tertiary amine groups do. It is believed that these primary and secondary amine groups arise in the end product from the reductive amination of the polyketones with secondary amines due to the disproportionation of the secondary amines under the conditions of the reaction to ammonia, a primary, a secondary, and even a tertiary amine, whose substituent radicals are, of course, those of the initially charged secondary amine. The formation of ammonia and a primary amine in addition to the original secondary amine, of course, leads to the inclusion in the final product of primary and secondary amine groups as well as the sought-for tertiary amine groups. As far as is now known, the monomeric tertiary amine resulting from the disproportionation does not enter into reaction with the polyketone in any way and accordingly, does not occur, except as a possible contaminant, in the final polymeric product.

Example VI

Twenty-five (25) parts of octadecyl bromide is added to a solution of 18.3 parts of a poly-tertiary amine of N. E. 183 in a mixture of 90 parts of xylene and 40 parts of n-butanol. The poly-tertiary amine used had been previously prepared by the reductive amination with dimethylamine of another sample of the polyketone described in Example V. The reaction mixture is heated at the reflux (123° C.) for 24 hours and the solvents removed by distillation under reduced pressure. There is thus obtained from the parent ethylene/carbon monoxide polyketone through the intermediate poly-tertiary amine, a polymethylene dimethyloctadecyl quaternary ammonium bromide as a dark, amber-colored, brittle resin readily soluble in water.

The starting poly-tertiary polyamine, assuming that all the carbonyl groups in the original polyketone are converted to extralinear tertiary amine groups with dimethylamine, should contain 13.9% nitrogen. Analytical determinations show the starting polyamine to contain 8.73% nitrogen, which figure indicates the conversion of 63% of the carbonyl groups in the parent polyketone to tertiary amine groups, assuming that all the nitrogen present in the poly-tertiary amine is, in fact, resident in tertiary amine groups. On this basis, the conversion of all the tertiary amine groups present in the starting polymeric poly-tertiary polyamine to quaternary ammonium bromide salt groups with octadecyl bromide would require the final polymeric quaternary ammonium bromide salt to contain 16.7% bromine. Analytical results show the polymethylene dimethyl octadecyl quarternary ammonium bromide product contains 13.9% bromine, thus, indicating on this basis the conversion of 83% of the tertiary amine groups to quaternary ammonium bromide salt groups. Thus, the final product contains, using the above assumptions, 37% of the original carbonyl groups of the starting polyketone, 17% of the tertiary amine groups (i. e., 17% of 63% or 10.7% of the original carbonyl groups in the parent polyketone as extralinear tertiary amine groups carrying two methyl substituents directly bonded to the nitrogen) and 83% of the tertiary amine groups as quaternary ammonium bromide groups (i. e., 83% of 63% or 52.3% of the original carbonyl groups of the parent polyketone as extralinear quaternary ammonium bromide groups carrying two methyl, one octadecyl, one bromide radical directly bonded to the extralinear nitrogen).

Example VII

Thirty-two (32) parts of methyl cyclohexanesulfonate is added to a solution of 42.2 parts of a polytertiary amine of N. E. 211 in a mixture of 270 parts of benzene and 80 parts of absolute ethanol. The poly-tertiary amine used had been previously prepared by the reductive amination with morpholine of another sample of the polyketone described in Example V. The solution is allowed to stand at room temperature for six days and the solvents then removed by distillation under reduced pressure. There is thus obtained from the parent ethylene/carbon monoxide polyketone 70 parts (91% conversion based on the intermediate poly-tertiary amine) of the polymethylene methyl morpholino quaternary ammonium cyclohexanesulfonate as a brown, brittle resin soluble in water.

The starting poly-tertiary polyamine, assuming that all the carbonyl groups in the original polyketone are converted to extralinear tertiary amine groups with morpholine, should contain 9.8% nitrogen. Analytical determinations show the starting polyamine to contain 7.1% nitrogen, which figure indicates the conversion of 72% of the carbonyl groups in the parent polyketone to tertiary amine groups, assuming that all the nitrogen present in the poly-tertiary amine is, in fact, resident in tertiary amine groups. On this basis, the conversion of all the tertiary amine groups present in the starting polymeric poly-tertiary polyamine to quaternary ammonium cyclohexanesulfonate salt groups with methyl cyclohexanesulfonate would require the final polymeric quaternary ammonium cyclohexanesulfonate salt to contain 9.2% sulfur. Analytical results show the polymethylene methyl morpholino quaternary ammonium cyclohexanesulfonate product to contain 7.7% sulfur, thus, indicating on this basis the conversion of 84% of the tertiary amine groups to quaternary ammonium cyclohexanesulfonate salt groups. Thus, the final product contains, using the above assumptions, 28% of the original carbonyl groups of the starting polyketone, 16% of the tertiary amine groups (i. e., 16% of 72% or 11.7% of the original carbonyl groups in the parent polyketone as extralinear tertiary amine groups having two of the valences of the nitrogen filled and joined through a 3-oxapentamethylene-1,5-di radical, i. e., the extralinear nitrogen is the nitrogen of a morpholine ring), and 84% of the tertiary amine groups as quaternary ammonium cyclohexanesulfonate groups (i. e., 84% of 72% or 60.3% of the original carbonyl groups of the parent polyketone as extralinear quaternary ammonium cyclohexanesulfonate groups carrying one methyl and one cyclohexanesulfonate radical directly attached to the extralinear nitrogen, the two remaining valences of which are together

joined in a morpholine ring, i. e., are filled by a 3-oxapentamethylene-1,5-di radical).

Example VIII

Thirteen and five-tenths (13.5) parts of triethylphosphate are added to a solution of a poly-tertiary amine of N. E. 281 in a mixture of 90 parts of xylene and 40 parts of isopropyl alcohol. The poly-tertiary amine used had been previously prepared by the reductive amination with morpholine of an ethylene/carbon monoxide polyketone of molecular weight 1600 containing ethylene and carbon monoxide in a 6.0:1 combined mole ratio. The resulting solution is refluxed at about 90° C. for about 24 hours and the solvents removed by distillation under reduced pressure. There is thus obtained from the parent ethylene/carbon monoxide polyketone—through the intermediate poly-tertiary amine—a polymethylene ethyl morpholino quaternary ammonium ethyl phosphate as a straw-colored, viscous liquid partially soluble in dilute acetic acid and of limited solubility in water.

The starting poly-tertiary polyamine, assuming that all the carbonyl groups in the original polyketone are converted to extralinear tertiary amine groups with morpholine, should contain 5.2% nitrogen. Analytical determinations show the starting polyamine to contain 5.1% nitrogen, which figure indicates the conversion of 98% of the carbonyl groups in the parent polyketone to tertiary amine groups, assuming that all the nitrogen present in the poly-tertiary amine is, in fact, resident in tertiary amine groups. On this basis, the conversion of all the tertiary amine groups present in the starting polymeric poly-tertiary polyamine to quaternary ammonium diethyl phosphate salt groups with triethyl phosphate would require the final polymeric quaternary ammonium diethyl phosphate salt to contain 6.9% phosphorus. Analytical results show the polymethylene ethyl morpholino quaternary ammonium diethyl phosphate product to contain 1.2% phosphorus, thus, indicating on this basis the conversion of 17% of the tertiary amine groups to quaternary ammonium diethyl phosphate salt groups. Thus, the final product contains, using the above assumptions, 2% of the original carbonyl groups of the starting polyketone, 83% of the tertiary amine groups (i. e., 83% of 98% or 81.3% of the original carbonyl groups in the parent polyketone as extralinear tertiary amine groups having two of the valences of the nitrogen filled and joined through a 3-oxapentamethylene-1,5-di radical, i. e., the extralinear nitrogen is the nitrogen of a morpholine ring), and 17% of the tertiary amine groups as quaternary ammonium diethyl phosphate groups (i. e., 17% of 98% or 16.7% of the original carbonyl groups of the parent polyketone as extralinear quaternary ammonium diethyl phosphate groups carrying one ethyl and one diethyl phosphate radical directly attached to the extralinear nitrogen, the two remaining valences of which are together joined in a morpholine ring, i. e., are filled by a 3-oxapentamethylene-1,5-di radical).

The monoolefin/carbon monoxide copolymers reductively aminated with secondary amines to form the polymeric polytertiary amines used as the starting materials for preparing the preferred products of this invention are formed by polymerizing at least one monoolefin containing from 2 to 4 carbon atoms, such as ethylene, propylene, isobutylene, or a plurality of said monoolefins with carbon monoxide in the presence of a suitable polymerization catalyst, for example, a peroxy compound, as disclosed and claimed in Patent No. 2,495,286 of M. M. Brubaker.

These monoolefin/carbon monoxide polyketones contain combined monoolefins and carbon monoxide in the mole ratio ranging from 1:1 to 150:1 and preferably from 1:1 to 50:1, and may contain other combined monomers such as vinyl chloride, vinyl acetate, styrene and other vinyl compounds; methyl methacrylate and other vinylidene compounds; dimethyl maleate, maleic anhydride, and other vinylene compounds and the like. These monoolefin/carbon monoxide polyketones range in molecular weight from 250 to 10,000 or higher. The polymers ranging in molecular weight from 1,000 to 3,000 and having a combined monoolefin/carbon monoxide mole ratio of from 1.5:1 to 10:1 are preferred for use in making the poly-tertiary polyamine starting products necessary in the preparation of the preferred products of this invention since such polymers are much more readily prepared. Furthermore, the poly-quaternary ammonium salts therefrom derived are of greater utility because of their increased solubility and better flexibility, softness, and lower melting point.

The properties of the polymeric quaternary ammonium salts of this invention vary as a function of the amount of carbonyl groups in the parent polyketone converted to tertiary amine groups, the nature of the substituents on the tertiary amine groups, the degree of the conversion of these tertiary amine groups to quaternary ammonium salts, and, in the case of the preferred products from the monoolefin/carbon monoxide polyketone, the combined monoolefin/carbon monoxide mole ratio.

A typical preparation of a monoolefin/carbon monoxide polyketone used in preparing the starting polytertiary polyamines necessary for the preparation of the preferred polymeric quaternary ammonium salts of this invention is given below, utilizing an ethylene/carbon monoxide polyketone:

A 10/1 molar ratio mixture of ethylene and carbon monoxide is prepared in a reservoir cylinder by introducing carbon monoxide to a pressure of 565 lb./sq. in. and finally introducing ethylene to a total pressure of 600 atmospheres. The mixed gases are displaced from this reservoir by water from a variable speed high pressure piston pump. A second pump is arranged to deliver a 0.471% solution of di-tertbutyl peroxide in benzene. These two streams are combined in a T-block, passed through a short section of unheated tubing to insure thorough mixing and finally enter into the reaction coil which is immersed in an oil bath at 175° C. The pumping rates are adjusted to provide a combined feed comprising 15% of the ethylene/carbon monoxide gas mixture, 0.15% di-tert-butyl peroxide and 84.85% of benzene and to permit a contact time of approximately 8 minutes in the heated reactor coil. The pressure on the entire system is maintained at 600 atmospheres by manual control of the discharge rate through one of two pressure control valves located at the end of the reactor coil. The product is expanded into collecting vessels arranged to permit bottom discharge of the liquid polymer solution while unreacted gases are expanded from the top to pass in turn through a liquid-gas separator, a wet test meter, a rotameter and finally to waste.

The liquid product collected is a homogeneous

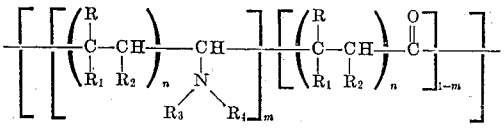
solution from which the polymeric product is isolated by evaporation of the benzene solvent at 80–85° C. under reduced pressure. The resulting polyketone is a firm, white wax comprising ethylene and carbon monoxide in 3.6/1 mole ratio and having an average molecular weight of 1180. This final product is obtained at an average conversion of 22% based on the total weight of ethylene and carbon monoxide pumped to the unit.

The poly-tertiary polyamines, whose quaternary ammonium salts constitute the preferred products of the present invention, are obtained by the hydrogenation in the presence of at least one secondary amine of the monoolefin/carbon monoxide polymers described in more detail in the previous paragraphs. According to one embodiment, the reductive amination is effected by bringing into intimate contact the polyketone, hydrogen, and at least one secondary amine in the presence of a suitable hydrogenation catalyst, which is effective for the reduction of oxocarbonyl groups. The reaction is carried out at temperatures between 50–300° C., and generally between 150 and 250° C., under a total pressure in excess of 20 atm., and preferably in the range of 40 to 1500 atm. The catalyst is used in amounts of from 0.005 to 20% and usually from 0.2 to 10% by weight of the polyketone. The secondary amine or amines are used in amounts of at least one mole, and usually from 2 to 12 moles, for every carbonyl group in the polyketone which it is desired to convert to a tertiary amine. The preparation and properties of these polymeric poly-tertiary polyamines are described in greater detail in Hoehn U. S. Patent No. 2,495,255.

A typical preparation of one of the poly-tertiary polyamines used in preparing the preferred polymeric quaternary ammonium salts of this invention is given below:

A mixture of 50 parts of an ethylene/carbon monoxide polyketone of molecular weight 1180 containing ethylene and carbon monoxide in a combined mole ratio of 3.6:1, 5 parts of a nickel-on-kieselguhr hydrogenation catalyst, and 100 parts of dimethylamine is charged into a silver-lined, steel, high pressure reaction vessel of internal capacity corresponding to 400 parts of water. The reaction is closed, placed in a shaking machine, and connected to a source of hydrogen under high pressure. It is then heated to 200° C. and agitated under 900–1,000 atm. hydrogen pressure for a period of 15 hours. The reactor is allowed to cool to room temperature, vented to the atmosphere, opened and the product removed and dissolved in benzene. The catalyst is removed by filtration and the filtrate then concentrated by distillation under reduced pressure, thereby removing the benzene solvent and any unreacted dimethylamine. There is thus obtained from the parent ethylene/carbon monoxide polyketone the N,N-dimethyl poly-tertiary amine as a light, straw-colored, soft grease readily soluble in dilute acetic acid. This poly-tertiary amine is determined by analysis to contain 5.88% nitrogen (by the Dumas procedure) and to exhibit a N. E. of 277. In theory, assuming each carbonyl group in the polyketone were to be converted to a tertiary amine group, the final product should contain 8.9% nitrogen. Thus, the above nitrogen analysis, neglecting the previously discussed possibility of the presence of primary and secondary amine groups, corresponds to a conversion of 66% of the carbonyl groups in the original polyketone to tertiary amine groups.

In the preferred polyamines, namely, those prepared by the reductive amination of the polyketones obtained by the copolymerization of 2 to 4 carbon monoolefins and carbon monoxide, the recurring groups have the formula:



wherein R, R_1 and R_2 are hydrogen or lower alkyl radicals of from 1 to 2 carbon atoms and the total number of carbons, if any, contained in R, R_1 and R_2 taken together cannot exceed 2, i. e., is less than 3, i. e., ranges from 0 to 2; R_3 and R_4 are aliphatic or cycloaliphatic, monovalent hydrocarbon radicals of from 1 to 18 carbons each which may be alike or different and may together be joined in a ring, preferably of 5 to 6 ring members, in which instance there may be a chalcogen of atomic weight less than 33, i. e., oxygen, or sulfur, present in the ring structure; n is a number from 1 to 150 and preferably from 1.5 to 10; and m is a number from 0.25 to 1. These polymers can vary in molecular weight from 250 to 10,000 or higher and preferably from 500 to 5,000 or higher.

The secondary amines useable in preparing the poly-tertiary amine starting materials necessary for the preparation of the preferred products of this invention, i. e., the poly-quaternary ammonium salts from the poly-tertiary polyamines prepared by the reductive amination of monoolefin/carbon monoxide polyketones, are aliphatic, cycloaliphatic, and saturated heterocyclic secondary monoamines wherein the two radicals attached to the nitrogen contain no more than eighteen carbons each and may be alike or different and may together be joined in a ring, preferably of 5 to 6 ring members, in which instance there may be a chalcogen of atomic weight less than 33, i. e., oxygen, or sulfur, present in the ring structure. Specific illustrations of these secondary monoamines are dialiphatic secondary monoamines, such as, diethyl-, dimethyl-, di-n-propyl-, diisopropyl-, di-n-amyl-, dioctyl-, didecyl-, didodecyl-, ditetradecyl-, dihexadecyl, dioctadecyl, N - methylethyl-, N - ethylpropylamines; dicycloaliphatic secondary monoamines, such as dicyclohexylamine; aliphatic cycloaliphatic secondary monoamines, such as N-ethylcyclohexylamine; cyclic secondary aliphatic monoamines in which the heterocycle contains—other than the amino nitrogen—solely carbon, such as piperidine; cyclic secondary monoamines in which the heterocycle—in addition to the amino nitrogen—contains carbon and a chalcogen of atomic weight less than 33, such as those wherein the chalcogen is oxygen, e. g., pyrrolidine and tetrahydro-1,4-(2)oxazine and those wherein the chalcogen is sulfur, such as tetrahydro-1,4-thiazine. Because of their low cost and readier availability, the dialiphatic secondary monoamines, wherein the two radicals on the nitrogen carry no more than 8, and preferably no more than 4 carbon atoms, each are particularly preferred.

The esters of organic alcohols and organic or inorganic acids useable in preparing the polymeric quaternary ammonium salts of this invention from the extralinear polytertiary polyamines are those of mono- or polybasic organic or inorganic acids of K_1 greater than 1.6×10^{-5} and hydrocarbon alcohols of from 1 to 18 carbons wherein the alcoholic hydroxyls are bonded di-

rectly to aliphatic carbon, said aliphatic carbon carrying, in addition, only hydrogen and/or hydrocarbon radicals, preferably aliphatically saturated. Specific examples of these include the alkyl esters of inorganic monobasic acids, such as methyl chloride, ethyl chloride, octadecyl bromide; the cycloalkyl esters of monobasic acids, such as, cyclohexyl bromide; the aralkyl esters of inorganic monobasic acids, such as, benzyl iodide; alkyl esters of polybasic inorganic acids, such as, dimethyl sulfate and triethyl phosphate; alkyl esters of organic monobasic acids, such as methyl formate and octyl acetate; alkyl esters of polybasic organic acids, such as methyl cyclohexanesulfonate; olefinically unsaturated esters of monobasic inorganic acids, such as allyl chloride, allyl bromide; esters of alkyl polyalcohols and monobasic inorganic acids, such as, 1,4-dichlorobutane; esters of olefinically unsaturated polyalcohols and monobasic inorganic acids, such as 1,4-dichlorobutene-2. These latter type polyesters of polyalcohols are, of course, capable of quaternization through all of the ester groups and accordingly are capable of forming cross-linked products. Due to the lack of complicated side reactions, it is preferred to use the esters of mono- or polybasic organic or inorganic acids of K_1 greater than 1.6×10^{-5} with aliphatically saturated hydrocarbon monoalcohols of 1 to 18 carbons wherein the alcoholic hydroxyls are directly bonded to aliphatic carbon, said aliphatic carbon carrying, in addition, only hydrogen and/or aliphatically saturated hydrocarbon radicals.

Polymeric quaternary ammonium salts of this invention are generally water-soluble, glassy resins or powdery solids. Their physical form depends upon the relative proportion of salt groups in their composition, i. e., the degree of conversion of the tertiary amine groups to quaternary ammonium salt groups, the molecular weight of the starting polyamine and in the case of the monoolefin/carbon monoxide derivatives, the mole ratio of combined monoolefin to carbon monoxide. For appreciable change in the properties of the poly-tertiary amines, it is necessary that at least 10% of the tertiary amine groups in the starting polymeric polyamine be converted to quaternary ammonium salt groups.

In this connection, it should be pointed out, of course, that it is not necessary that the starting polyamines contain solely tertiary amine groups. As discussed previously in the specification, the polytertiary amines contain minor proportions of primary and secondary amine groups. Furthermore, it is within the scope of this invention to reductively aminate a monoolefin/carbon monoxide polyketone or a polymeric vinyl ketone polymer or copolymer with a mixture of ammonia, primary, and secondary amines in the presence of hydrogen, thus preparing an end product containing primary, secondary and tertiary amine groups as extralinear substituents of the main polymer chain. Such a product can easily be converted with one of the above-described esters of an organic alcohol and an inorganic or organic acid to a poly-quaternary ammonimum salt of this invention. For such products to exhibit the properties characteristic of these new polymeric quaternary ammonium salts, it is desirable that at least 25% and preferably 50% of the carbonyl groups in the original polymer be converted to tertiary amine groups, and secondly, that at least 10% of these tertiary amine groups be converted into quaternary ammonium salt groups.

The new polmeric quaternary ammonium salts of this invention, especially the preferred polymeric quaternary ammonium salts prepared from the polymeric poly-tertiary polyamines obtained by the reductive amination of monoolefin/carbon monoxide polyketones, are useful as bactericides and fungicides, as antisnag finishes for nylon hosiery and in other textile applications, for instance, modifiers for viscose and antistatic agents for nylon. The new polymeric quaternary ammonium salts of this invention are also useful as detergents in the dry-cleaning industry—a particularly outstanding and useful application since their use in conjunction with conventional dry cleaning agents markedly increases the effectiveness of the cleansing procedure.

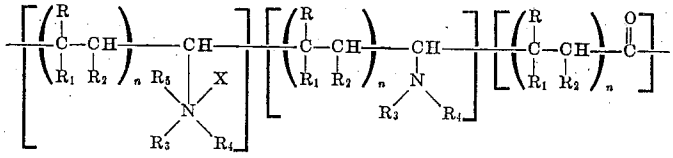
As many apparently widely different embodiments of this invention may be made without departing from the spirit and scope thereof, it is to be understood that this invention is not limited to the specific embodiments thereof except as defined in the appended claims.

I claim:

1. A polymeric poly-quaternary ammonium salt having a molecular weight of at least 500 and a main polymer chain of contiguous aliphatic carbon atoms and consisting of the recurring structural units: (*a*) groups containing at least three contiguous carbon atoms of which one is carbonyl carbon and at least the next two contiguous carbon atoms are saturated aliphatic hydrocarbon and are an integral part of the main polymer chain, (*b*) groups containing at least three continguous carbon atoms of which one is connected to an extralinear amino nitrogen and at least the next two contiguous carbon atoms are saturated aliphatic hydrocarbon and are an integral part of the main polymer chain, the remaining valences of said amino nitrogen atom being satisfied by members selected from the class consisting of cycloaliphatic and aliphatic monovalent saturated hydrocarbon radicals of up to 18 carbon atoms, saturated aliphatic hydrocarbon radicals joined to each other to form with said amino nitrogen atom a 5- to 6-membered ring, and saturated aliphatic hydrocarbon radicals joined to each other through a chalcogen of atomic weight less than 33 to form with said amino nitrogen atom a 5- to 6-membered ring, and (*c*) groups containing at least three contiguous carbon atoms of which one is connected to an extralinear quaternary ammonium nitrogen atom and at least the next two contiguous carbon atoms are saturated aliphatic hydrocarbon and are an integral part of the main polymer chain, two of the valences of said quaternary ammonium nitrogen atom being satisfied by members selected from the class consisting of cycloaliphatic and aliphatic monovalent saturated hydrocarbon radicals of up to 18 carbon atoms, saturated aliphatic hydrocarbon radicals joined to each other to form with said quaternary ammonium nitrogen atom a 5- to 6-membered ring, and saturated aliphatic hydrocarbon radicals joined to each other through a chalcogen of atomic weight less than 33 to form with said quaternary ammonium nitrogen atom a 5- to 6-membered ring, another valence of said quaternary ammonium nitrogen atom being satisfied by the anion of an acid having a primary acid ionization constant K_1 greater than 1.6×10^{-5}, the remaining valence of said quater-

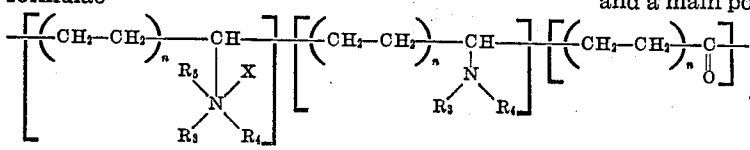
nary ammonium nitrogen atom being satisfied by a monovalent hydrocarbon radical of not more than 18 carbon atoms and having an aliphatic carbon atom directly connected to said quaternary ammonium nitrogen atom, at least 25% of said recurring structural units being those of groups (*b*) and (*c*) containing a nitrogen atom, of which at least 10% are those of group (*c*) containing the quaternary ammonium nitrogen atom.

2. A polymeric poly-quaternary ammonium salt having a molecular weight of at least 500 and a main polymer chain of contiguous aliphatic carbon atoms and consisting of the recurring structural units having the following formulae



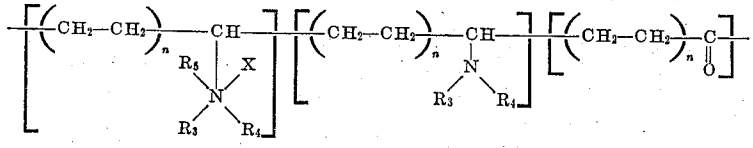
wherein R, R_1 and R_2 are members of the class consisting of hydrogen and lower alkyl radicals of from 1 to 2 carbon atoms, the sum of the carbon atoms in R, R_1 and R_2 not exceeding 2, R_3 and R_4 are members of the class consisting of cycloaliphatic and aliphatic monovalent saturated hydrocarbon radicals of up to 18 carbon atoms, saturated aliphatic hydrocarbon radicals joined to each other to form with the nitrogen atom a 5- to 6-membered ring, and saturated aliphatic hydrocarbon radicals joined to each other through a chalcogen of atomic weight less than 33 to form with the nitrogen atom a 5- to 6-membered ring, X is the anion of an acid having a primary acid ionization constant K_1 greater than 1.6×10^{-5}, R_5 is a monovalent hydrocarbon radical of not more than 18 carbon atoms and having an aliphatic carbon atom directly connected to the nitrogen atom, *n* is a number from 1 to 150, at least 25% of said recurring structural units are those of the structural formulae containing a nitrogen atom, of which at least 10% are those of the structural formula containing the quaternary ammonium nitrogen atom.

3. A polymeric poly-quaternary ammonium salt having a molecular weight of at least 500 and a main polymer chain of contiguous aliphatic carbon atoms and consisting of the recurring structural units having the following formulae



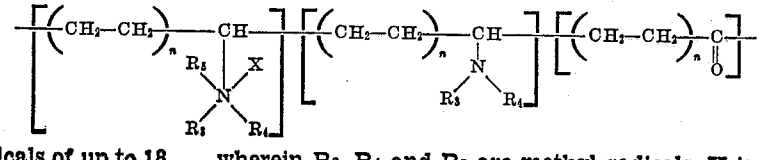
wherein R_3 and R_4 are members of the class consisting of cycloaliphatic and aliphatic monovalent saturated hydrocarbon radicals of up to 18 carbon atoms, saturated aliphatic hydrocarbon radicals joined to each other to form with the nitrogen atom a 5- to 6-membered ring, and saturated aliphatic hydrocarbon radicals joined to each other through a chalcogen of atomic weight less than 33 to form with the nitrogen atom a 5- to 6-membered ring, X is the anion of an acid having a primary acid ionization constant K_1 greater than 1.6×10^{-5}, R_5 is a monovalent hydrocarbon radical of not more than 18 carbon atoms and having an aliphatic carbon atom directly connected to the nitrogen atom, *n* is a number from 1 to 150, at least 25% of said recurring structural units are those of the structural formulae containing a nitrogen atom, of which at least 10% are those of the structural formula containing the quaternary ammonium nitrogen atom.

4. A polymeric poly-quaternary ammonium salt having a molecular weight of at least 1000 and a main polymer chain of contiguous aliphatic carbon atoms and consisting of the recurring structural units having the following formulae



wherein R_3 and R_4 are members of the class consisting of cycloaliphatic and aliphatic monovalent saturated hydrocarbon radicals of up to 18 carbon atoms, saturated aliphatic hydrocarbon radicals joined to each other to form with the nitrogen atom a 5- to 6-membered ring, and saturated aliphatic hydrocarbon radicals joined to each other through a chalcogen of atomic weight less than 33 to form with the nitrogen atom a 5- to 6-membered ring, X is the anion of an acid having a primary acid ionization constant K_1 greater than 1.6×10^{-5}, R_5 is a monovalent hydrocarbon radical of not more than 18 carbon atoms and having an aliphatic carbon atom directly connected to the nitrogen atom, *n* is a number from 1 to 10, at least 50% of said recurring structural units are those of the structural formulae containing a nitrogen atom, of which at least 10% are those of the structural formula containing the quaternary ammonium nitrogen atom.

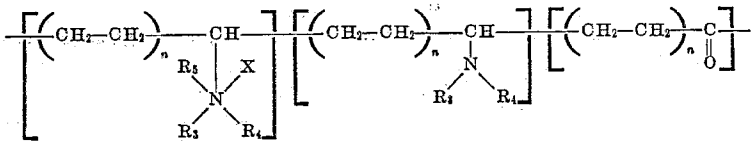
5. A polymeric poly-quaternary ammonium salt having a molecular weight of at least 1000 and a main polymer chain of contiguous aliphatic carbon atoms and consisting of the recurring structural units having the following formulae



wherein R_3, R_4 and R_5 are methyl radicals, X is

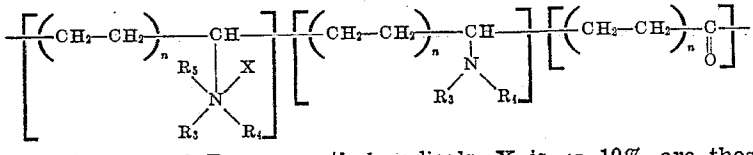
iodine, n is a number from 1 to 10, at least 50% of said recurring structural units are those of the structural formulae containing a nitrogen atom, of which at least 10% are those of the structural formula containing the quaternary ammonium nitrogen atom.

6. A polymeric poly-quaternary ammonium salt having a molecular weight of at least 1000 and a main polymer chain of contiguous aliphatic carbon atoms and consisting of the recurring structural units having the following formulae



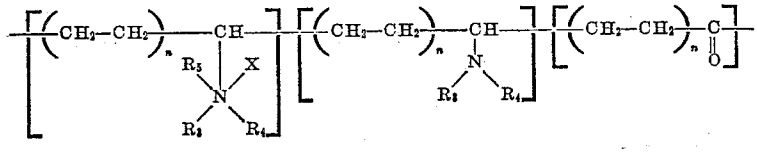
wherein R_3 and R_4 are methyl radicals, X is chlorine, R_5 is the benzyl radical, n is a number from 1 to 10, at least 50% of said recurring structural units are those of the structural formulae containing a nitrogen atom, of which at least 10% are those of the structural formula containing the quaternary ammonium nitrogen atom.

7. A polymeric poly-quaternary ammonium salt having a molecular weight of at least 1000 and a main polymer chain of contiguous aliphatic carbon atoms and consisting of the recurring structural units having the following formulae



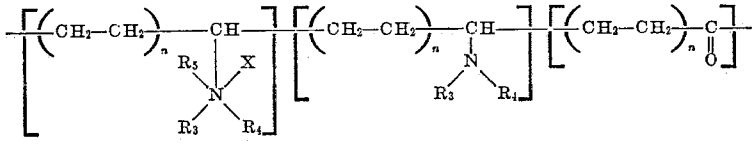
wherein R_3 and R_4 are methyl radicals, X is bromine, R_5 is the octadecyl radical, n is a number from 1 to 10, at least 50% of said recurring structural units are those of the structural formulae containing a nitrogen atom, of which at least 10% are those of the structural formula containing the quaternary ammonium nitrogen atom.

8. A polymeric poly-quaternary ammonium salt having a molecular weight of at least 1000 and a main polymer chain of contiguous aliphatic carbon atoms and consisting of the recurring structural units having the following formulae



wherein R_3 and R_4 are saturated aliphatic hydrocarbon radicals joined to each other through an oxygen atom to form with the nitrogen atom a 6-membered ring, X is the cyclohexanesulfonate radical, R_5 is the methyl radical, n is a number from 1 to 10, at least 50% of said recurring structural units are those of the structural formulae containing a nitrogen atom, of which at least 10% are those of the structural formula containing the quaternary ammonium nitrogen atom.

9. A polymeric poly-quaternary ammonium salt having a molecular weight of at least 1000 and a main polymer chain of contiguous aliphatic carbon atoms and consisting of the recurring structural units having the following formulae



wherein R_3 and R_4 are saturated aliphatic hydrocarbon radicals joined to each other through an oxygen atom to form with the nitrogen atom a 6-membered ring, X is the diethylphosphate radical, R_5 is the ethyl radical, n is a number from 1 to 10, at least 50% of said recurring structural units are those of the structural formulae containing a nitrogen atom, of which at least 10% are those of the structural formula containing the quaternary ammonium nitrogen atom.

DONALD D. COFFMAN.

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