

Description

The present invention relates to a polycationic compound which can react with hydrogen peroxide to give an organic peracid, being useful as an organic peracid precursor, and a bleach composition containing the same.

Prior Art

A chlorinated bleaching agent has the significant disadvantages insofar that the fibers to which it is applicable are limited, that it is not applicable to colored or patterned cloths and that it has a peculiar odor, though it exhibits a very high bleaching effect.

Therefore, an oxygenic bleaching agent free from these disadvantages has recently been used widely.

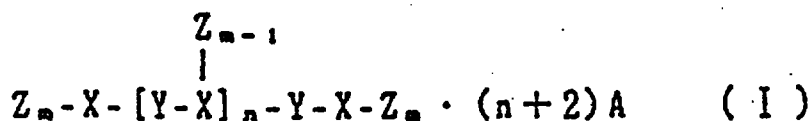
As such an oxygenic bleaching agent, sodium percarbonate and sodium perborate are particularly preferably useful from the standpoint of bleaching performance and storage stability.

Although the oxygenic bleaching agent is applicable to colored or patterned cloths in contrast to the chlorinated bleaching agent, the bleaching power thereof is so poor that the use of various bleach activators which are convertible into an organic peracid having a higher oxidation-reduction potential has been attempted. EP-A-303520 discloses studies on various bleach activators including nitriles such as acetonitrile, malononitrile, phthalonitrile and benzoyliminodiacetonitrile; O-acetyl compounds such as glucose pentaacetate, octaacetylsucrose, triacetin, sorbitol hexaacetate, acetoxymethanesulfonate salt, triacetyl cyanurate and methyl chloroformate; N-acetyl compounds such as N,N,N',N'-tetraacetylenediamine, di-n-acetyldimethylglyoxime, 1-phenyl-3-acetylhydantoin, N,N-diacetylaniline, N-acetyldiglycolimide and diacetylmethylenediformamide; acid anhydrides such as phthalic, succinic, benzoic, glutaric and alkylsulfuric anhydrides and mixed anhydrides of carboxylic acids with organosulfonic acids; sulfonyl oximes such as di-(methanesulfonyl)dimethylglyoxime; acylated phosphate salts such as diethylbenzoyl phosphate salts; phenyl sulfonate esters; organophosphoric acid azides such as diphenylphosphinic azide; disulfones such as diphenyl disulfone; N-sulfonylimidazole; cyanamides; halogenated triazines and N,N-dimethyl-N-octyl-N-10-carbophenoxydodecylammonium chloride. However, the bleaching powder is insufficient as yet, even if such a bleach activator is used simultaneously.

Disclosure of the invention

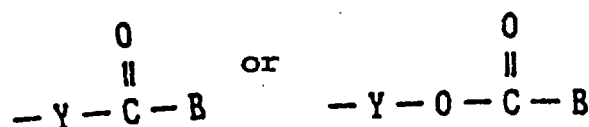
The inventors of the present invention have intensively studied to obtain a higher-performance oxygenic bleaching agent and have found that when a peroxide and a polyamine derivative as an organic peracid precursor are used simultaneously, the formed organic peracid is concentrated on the surface of a cloth to give a remarkably enhanced bleached effect. The present invention has been accomplished on the basis of this finding.

Namely, the present invention provides a new polycationic compound useful as an organic peracid precursor represented by the following general formula (I),



wherein

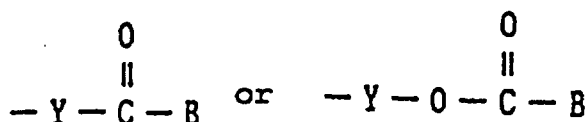
- X: an N^+ cationic group,
 Y: an alkylene group having 1 to 9 carbon atoms, which may be substituted with a hydroxyl group or a $-(C_2H_4O)_{1-5}-C_2H_4-$ or $-(C_3H_6O)_{1-5}-C_3H_6-$ group, wherein a plurality of Y groups may be the same or different from each other,
 Z: an



group,

(wherein B will be defined below), an alkyl group having 1 to 20 carbon atoms or an alkenyl group, each of which may be substituted with a hydroxyl group, or a

-(C₂H₄O)₁₋₅-H or -(C₃H₅O)₁₋₅-H group, with the proviso that at least one Z group is a



group,

though the Z groups may be the same or different from each other,

m: is 3 with respect to the Z_m or Z_{m-1} groups bonded to the X group,

n: a number of 0 to 3,

A: an inorganic or organic anionic group, with the proviso that A is absent when Z and X are combined together to form an inner salt, wherein a plurality of A groups may be the same or different from each other,

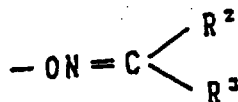
wherein a plurality of the above B groups represent each any of the following groups and may be the same or different from each other in one molecule:

a)



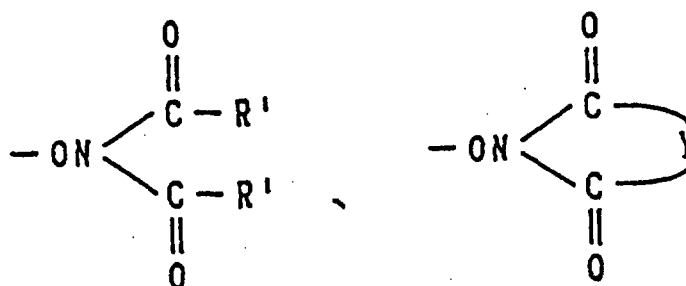
(wherein p and q each represent -H, -SO₃M, -COOM, -COOR¹, a halogen atom, -OR¹, or -N(R¹)₃ A, wherein M represents an alkali metal, an alkaline earth metal, an ammonium, an alkanolammonium or a negative charge necessary to build the inner salt, R¹ represents H, an alkyl group having 1 to 20 carbon atoms, an alkenyl or hydroxyalkyl group or a -(C₂H₄O)₁₋₅-H or -(C₃H₅O)₁₋₅-H group; A is as defined above and p and q may be the same or different from each other),

b) an oxime group having a structure represented by the formula

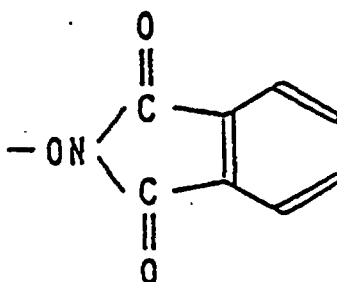


(wherein R² and R³ are the same as those defined above with respect to R¹ and may be the same or different from each other, with the proviso that at least one of R² and R³ must not be H),

c) an imidoxime group represented by the formula:



or



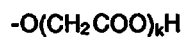
(wherein R^1 and Y are as defined above),

d) an alkanesulfonic acid group represented by the formula:



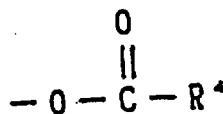
(wherein Y and M are as defined above),

e) a polyglycolic ester group represented by the formula:



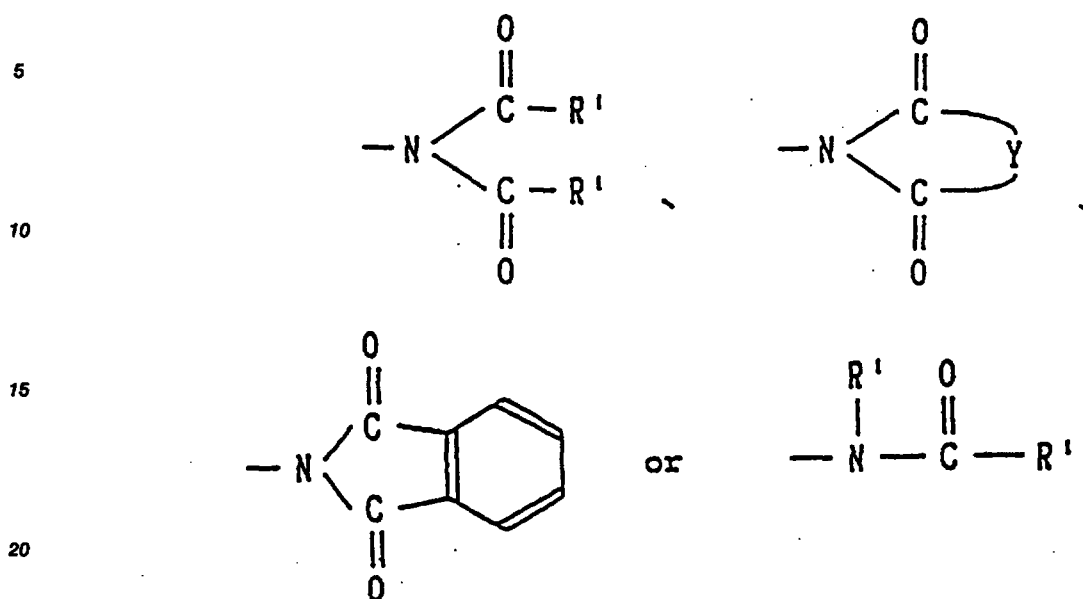
(wherein k is a number of 1 to 10),

f) an acid anhydride group represented by the formula:



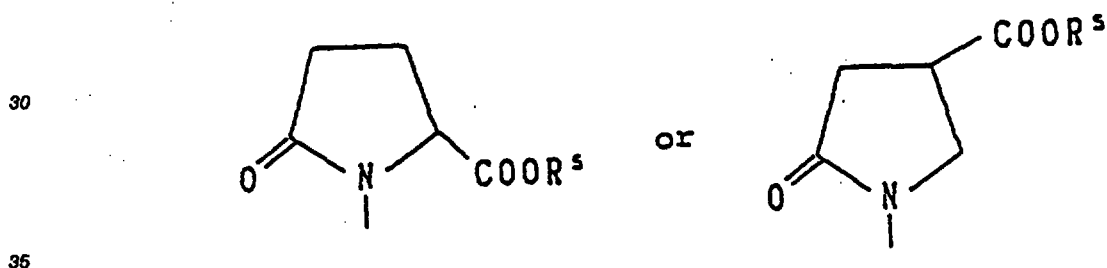
(wherein R^4 represents an alkyl group having 1 to 22 carbon atoms, an alkenyl group or a phenyl group which may be substituted),

g) an imide group represented by the formula:



(wherein R¹ and Y are as defined above)

h) a pyrrolidonecarboxylic acid derivative group represented by the formula:



(wherein R⁵ is the same as that defined above with respect to R¹ or M),

i) a ketone derivative group represented by the formula:

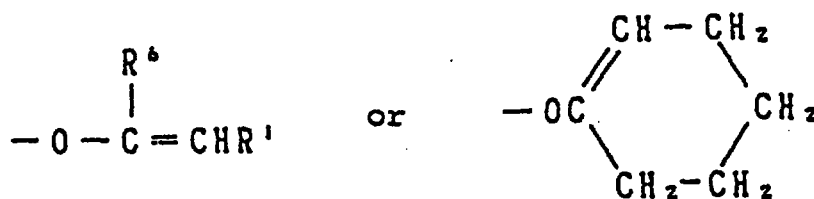


(wherein R¹ is as defined above and W is



55 -C=N, -NO₂ or -SO₂R¹, wherein a plurality of W groups may be the same or different from each other),

j) an enol derivative group represented by the formula:



(wherein R⁶ is the same as that defined above with respect to R¹ excepting H).

The bleach composition of the present invention contains a polycationic compound represented by the above general formula (I) as an organic peracid precursor. This polycationic compound reacts with a peracid anion generated from a peracid in water to give an organic peracid having a plurality of positive charges in one molecule and this organic peracid is highly efficiently concentrated on the surface of a cloth to exhibit a bleaching power dramatically improved as compared with that of the organic peracid of the prior art.

The peroxide which can generate a peracid anion reactive with the organic peracid precursor according to the present invention is preferably hydrogen peroxide or a peroxide which can generate hydrogen peroxide in an aqueous solution.

Examples of the peroxide which can generate hydrogen peroxide in an aqueous solution include organic and inorganic hydrogen peroxide adducts such as sodium carbonate/hydrogen peroxide adduct, sodium tripolyphosphate/hydrogen peroxide adduct, sodium pyrophosphate/hydrogen peroxide adduct, and 4Na₂SO₄ • 2H₂O₂ • NaCl; and inorganic peroxides such as sodium perborate monohydrate, sodium perborate tetrahydrate, sodium peroxide and potassium peroxide, among which sodium carbonate/hydrogen peroxide adduct, sodium perborate monohydrate and sodium perborate tetrahydrate are preferable.

In the bleach composition of the present invention, the peroxide and the organic peracid precursor are used at a molar ratio ranging from 99.9 : 0.1 to 20 : 80, preferably from 95 : 5 to 50 : 50. If the amount of the organic peracid precursor is below this range, only an insufficient effect will be attained, while even if the precursor is used in an amount above this range, the precursor will not act effectively to result in waste unfavorably.

The bleach composition of the present invention may contain known additives which are conventionally added to bleach compositions, in addition to the essential components described above. Examples of such additive include water-soluble inorganic builders such as sulfates, carbonates, bicarbonates, silicates and phosphates; and organic builders such as ethylenediamine-tetraacetate salts, tartrate salts and citrate salts. If necessary, the composition of the present invention may further contain an antiredeposition agent such as carboxymethylcellulose, polyvinylpyrrolidone or polyethylene glycol; various surfactant, enzyme, fluorescent whitening agent, dye, pigment or perfume.

Further, a bleaching detergent composition can be also prepared by suitably blending a conventional powdered detergent for cloths with the organic peracid precursor and peroxide according to the present invention.

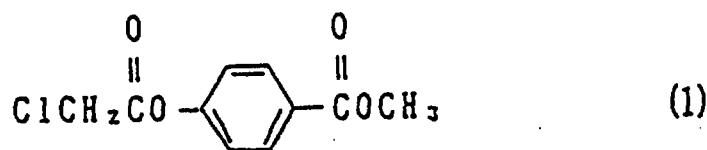
[Effect of the Invention]

The bleach composition of the present invention characterized by containing the new polycationic compound can exhibit a high bleaching power which cannot be attained by the oxygenic bleaching agents of the prior art including organic peracids.

[Example]

The present invention will now be described by referring to the following Examples, though the present invention is not limited to them.

5 <Referential Example 1...synthesis of compound (1)>



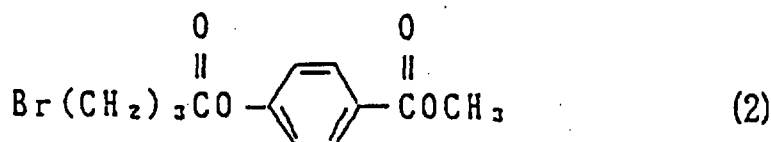
15 100 g of methyl p-hydroxybenzoate (MW: 152.15, 0.66 mol), 300 g of acetone and 66.5 g of triethylamine (MW: 101.2, 0.66 mol) were mixed together in a 1-l four-necked flask fitted with a condenser, a mechanical stirrer and a thermometer. 77.9 g of chloroacetyl chloride (MW: 112.9, 0.69 mol) were dropped into the flask over a period of about one hour, while keeping the flask on a water bath. The reaction mixture was aged for about 2 to 3 hours. Thereafter, the triethylamine hydrochloride thus precipitated was filtered away and the acetone was distilled off under a reduced pressure. The obtained residue was further distilled under the conditions of 66,5 Pa (0.5 mmHg) and 145 to 155 °C to give 144.8 g of the compound (1) represented by the above formula as a white solid.

MW: 228.6, yield: 70%, purity: 92%

20 IR (KBr cm⁻¹)

1776, 1722, 1605, 1503, 1284, 1200, 1161, 1110, 768

<Referential Example 2...synthesis of compound (2)>



The same procedure as that of Referential Example 1 was repeated except that 122.5 g of bromobutyryl chloride (MW: 185.6, 0.66 mol) were used instead of the chloroacetyl chloride. Thus, the compound (2) was obtained.

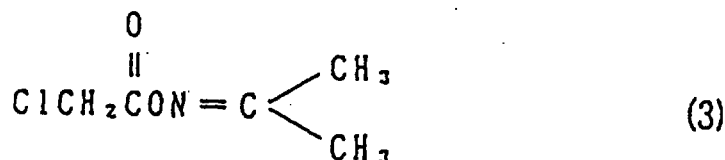
35 amount: 171.1 g, MW: 301.3, yield: 80%,

purity: 93%

IR (KBr cm⁻¹)

1752, 1731, 1608, 1506, 1278, 1197, 1140, 1110

40 <Referential Example 3...synthesis of compound (3)>



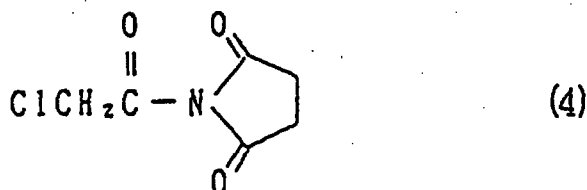
100 g of acetoxime (MW: 73.10, 1.37 mol), 150 g of tetrahydrofuran and 108.4 g of pyridine (MW: 79.1, 1.37 mol) were mixed together in a 1-l four-necked flask fitted with a condenser, a mechanical stirrer and a thermometer. 154.7 g of chloroacetyl chloride (MW: 112.9, 1.37 mol) were dropped into the flask over a period of about one hour, while keeping the flask on a water bath. The reaction mixture was aged for about 2 to 3 hours. The pyridine hydrochloride thus precipitated was filtered away and the tetrahydrofuran was distilled off. Thus, 149.5 g of the compound (3) was obtained.

MW: 149.5, yield: 90%, purity: 90%

IR (KBr cm^{-1})

3000, 2960, 2920, 1776, 1644, 1436, 1414, 1374, 1310, 1282, 1236, 1144, 1066, 928, 876, 784

(Referential Example 4...synthesis of compound (4))



15 100 g of succinimide (MW: 99, 1.01 mol), 150 g of dichloroethane and 114.0 g of chloroacetyl chloride (MW: 112.9, 1.01 mol) were placed in a 1-l four-necked flask fitted with a condenser, a mechanical stirrer and a nitrogen gas inlet tube and the temperature of the contents was raised to 80 to 85 °C under stirring. The reaction was carried out for about 5 to 10 hours, while removing the HCl gas generated as a by-product by introducing nitrogen into the flask. After the completion of the reaction, the disappearance of succinimide

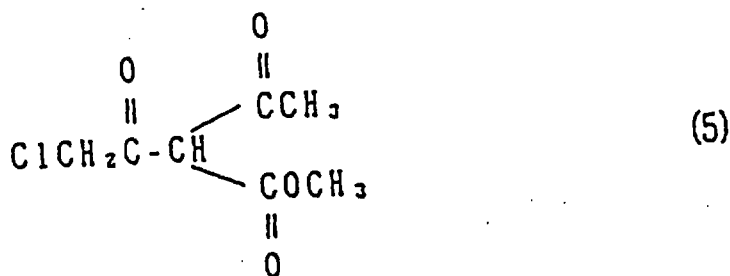
20 was confirmed by TLC and thereafter, the dichloroethane was distilled off. Thus, 152.7 g of the compound (4) was obtained.

yield: 75%, purity: 87%, MW: 175.4

IR (KBr cm^{-1})

1812, 1755, 1713, 1635

(Referential Example 5...synthesis of compound (5))



40 The compound (5) was prepared according to a variation of the method described in Ber., 67B, 935 (1934).

45 5.33 g (0.22 mol) of magnesium was placed in a 0.5-l four-necked flask, followed by the addition of 5 ml of absolute ethanol and 0.5 ml of carbon tetrachloride. After 2 or 3 minutes, 75 ml of absolute ethanol were carefully added thereto. Then, a mixture comprising 22.5 g of methyl acetoacetate (MW: 116.12, 0.22 mol), 25 ml of absolute ethanol and 25 ml of anhydrous ether was dropped into the flask, while heating the contents so as to reflux them mildly. The reaction mixture was aged for 3 hours and thereafter, 22.6 g of chloroacetyl chloride (MW: 112.9, 0.20 mol) were dropped into the flask over a period of about 30 minutes. The reaction mixture was again aged for 30 minutes and adjusted to pH 7 with 20% H_2SO_4 . The obtained ethereal layer was washed with water and freed from the ether by distillation. Thus, 34.1 g of the compound

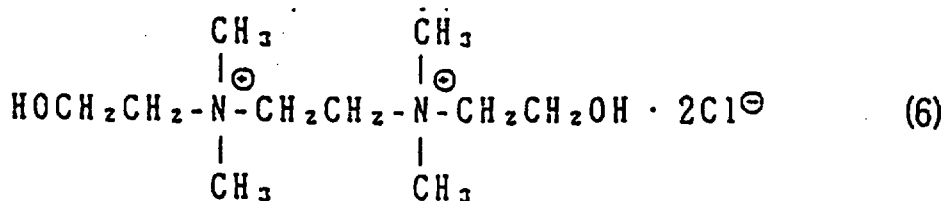
50 (5) was obtained.

yield: 52.0%, purity: 76%, MW: 226.3

IR (KBr cm^{-1})

2926, 2854, 1737, 1683, 1614, 1464, 1419, 1374, 1296, 1101, 774

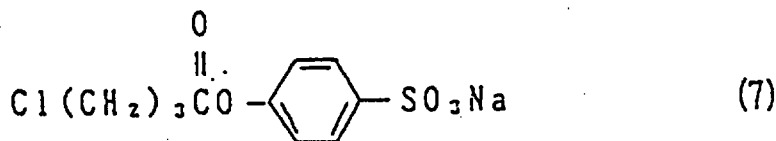
5 <Referential Example 6...synthesis of compound (6)>



15 116 g of N,N,N',N'-tetramethylethylenediamine (MW: 116, 1.0 mol) and 116 g of distilled water were mixed together in a 1-l four-necked flask fitted with a condenser, a thermometer, a mechanical stirrer and a dropping funnel, while keeping the flask in an ice bath. Thereafter, 208.6 g (2.0 mol) of a 35% aqueous solution of HCl were dropped into the flask through the dropping funnel over a period of about one hour. The reaction mixture was aged for 30 minutes and freed from the water by vacuum distillation with an evaporator to give 185 g of N,N,N',N'-tetramethylethylenediamine hydrochloride. 150 g of this hydrochloride (MW: 189, 0.79 mol), 150 g of dioxane and 73.0 g of ethylene oxide (MW: 44, 1.66 mol) were fed into a 1-l autoclave, which was purged with nitrogen several times. The reaction mixture was heated to 150°C and aged for 4 hours. After the completion of the reaction, the dioxane was distilled off and the obtained residue was recrystallized from acetone to give 203.2 g of the compound (6) (MW: 277, 0.72 mol).

yield: 91%, purity: 98%

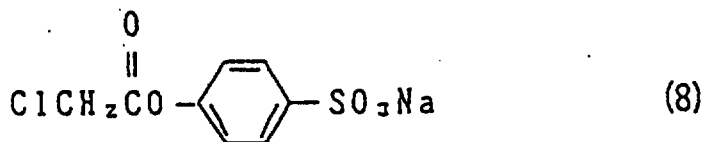
25 <Referential Example 7...synthesis of compound (7)>



35 100 g of disodium p-phenolsulfonate (prepared by neutralizing sodium p-phenolsulfonate with an equimolar amount of caustic soda and dehydrating the neutralization product, MW: 218.2, 0.46 mol) and 300 g of N,N-dimethylformamide were mixed together in a 1-l four-necked flask fitted with a condenser, a mechanical stirrer, a thermometer and a dropping funnel. 64.8 g of 4-chlorobutyryl chloride (MW: 140.9, 0.46 mol) were dropped into the flask over a period of about 2 hours, while keeping the flask in an ice bath. 40 The reaction mixture was aged for one hour and distilled under a reduced pressure to remove the N,N-dimethylformamide. The obtained solid was washed with acetone several times and dried to give 159 g of the compound (7).

MW: 300.6, yield: 85%, purity: 83.1%

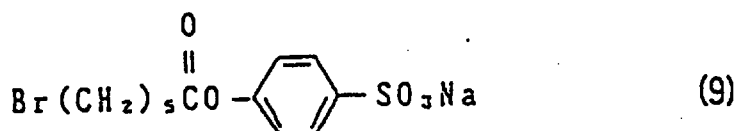
45 <Referential Example 8...synthesis of compound (8)>



55 The same procedure as in Referential Example 7 was repeated except that 51.9 g of monochloroacetyl chloride (MW: 112.9, 0.46 mol) were used instead of the 4-chlorobutyryl chloride. Thus, the compound (8) was obtained.

amount: 135.1 g, MW: 272.6, yield: 86%,
purity: 78.4%

(Referential Example 9...synthesis of compound (9))

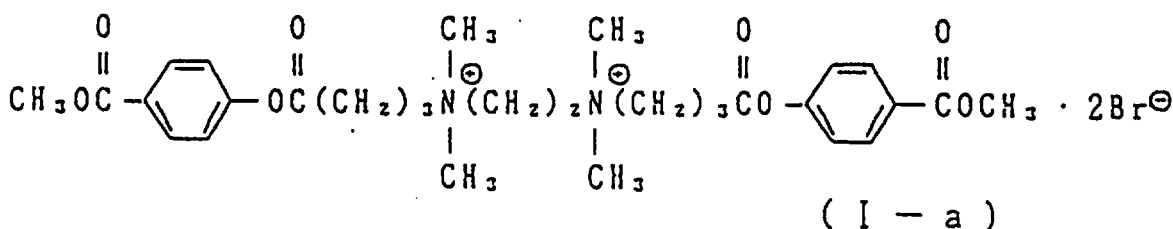


The same procedure as in Referential Example 7 was repeated except that 98.2 g of 6-bromocaproyl chloride (MW: 213.5, 0.46 mol) were used instead of the 4-chlorobutyryl chloride. Thus, the compound (9) was obtained.

amount: 181.7 g, MW: 373.2, yield: 80%,
purity: 75.6%

Example 1

synthesis of compound (I-a)



100 g of the compound (2) (MW: 301.3, purity: 93%, 0.31 mol), 300 g of acetone and 17.9 g of N,N,N',N'-tetramethylethylenediamine (MW: 116, 0.15 mol) were mixed together in a 1-l three-necked flask fitted with a condenser, a mechanical stirrer and a thermometer and heated so as to reflux the acetone mildly for about 20 hours to carry out a reaction. The disappearance of the amine was confirmed by titration with a 1/5 N aqueous solution of HCl (indicator: BCG). Thereafter, the reaction mixture was filtered. The obtained crystal was washed with acetone several times and dried to give 62 g of a white crystal (I-a).

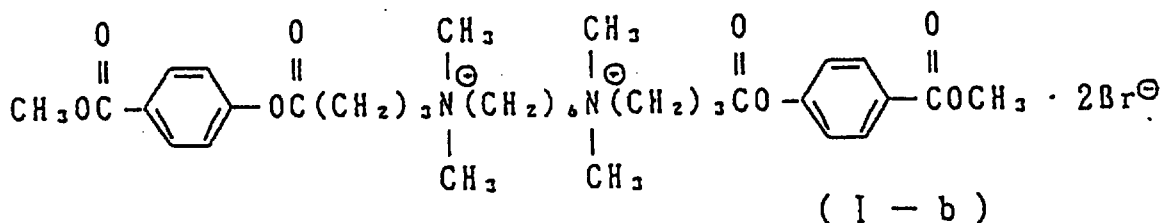
MW: 718.5, purity: 86%, yield: 49%

IR (KBr cm^{-1})

1755, 1722, 1608, 1437, 1416, 1377, 1281, 1203, 1161, 1110, 1014, 966, 909, 765

Example 2

synthesis of compound (I-b)



The same procedure as in Example 1 was repeated except that 25.8 g of N,N,N',N'-tetramethylhexamethylenediamine (MW: 172, 0.15 mol) were used instead of the N,N,N',N'-tetramethylethylenediamine.

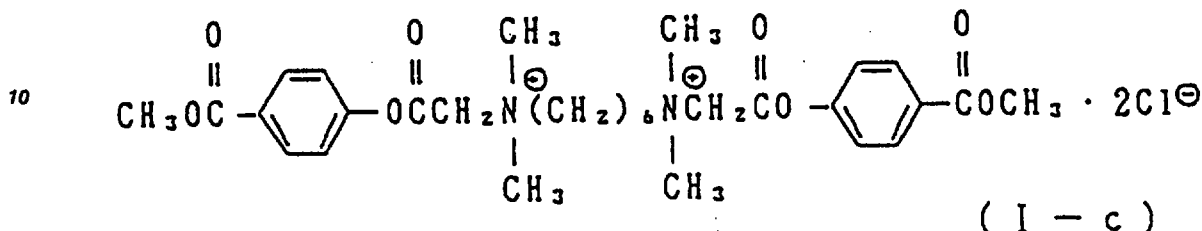
amount: 73.3 g, purity: 84%, yield: 53%

IR (KBr cm^{-1})

2956, 1755, 1722, 1605, 1440, 1377, 1284, 1203, 1161, 1014, 909, 861, 765, 699

Example 3

5 synthesis of compound (I-c)



The same procedure as in Example 2 was repeated except that 77.0 g of the compound (1) (MW: 228.6, purity: 92%, 0.31 mol) were used instead of the compound (2).

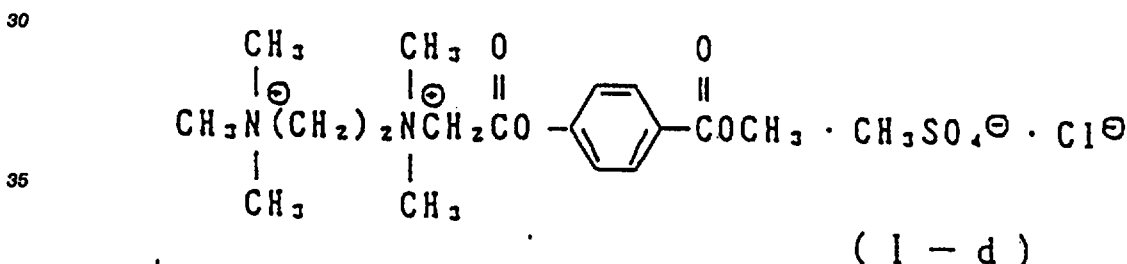
amount: 84.0 g, MW: 629.2, purity: 87.6%,
yield: 78.0%

IR (KBr cm^{-1})

3010, 2926, 2776, 1776, 1725, 1605, 1503, 1470, 1443, 1413, 1281, 1197, 1161, 1110, 1038, 1008, 996, 963, 900, 861, 798, 777, 732, 687, 507

Example 4

synthesis of compound (I-d)



37.3 g of the compound (1) (MW: 228.6, 0.15 mol, purity: 92%) and 150 g of dichloromethane were mixed together in a 1-l four-necked flask fitted with a condenser, a mechanical stirrer, a thermometer and a dropping funnel. 17.4 g of N,N,N',N'-tetramethylethylenediamine (MW: 116, 0.15 mol) were dropped into the flask through the dropping funnel over a period of 5 minutes, while keeping the flask in an ice bath. In this step, the exothermic reaction elevated the reaction temperature by about 15 to 20 °C. The reaction mixture was aged for 2 hours. Thereafter, 18.9 g of dimethyl sulfate (MW: 126.1, 0.15 mol) were dropped into the flask through the dropping funnel over a period of about one hour and the reaction was carried out for additional 2 hours. The crystals precipitated were recovered by filtration, washed with dichloromethane several times and dried to give 54.7 g of a white crystals (I-d).

purity: 87%, yield: 67.4%, MW: 470.7

IR (KBr cm^{-1})

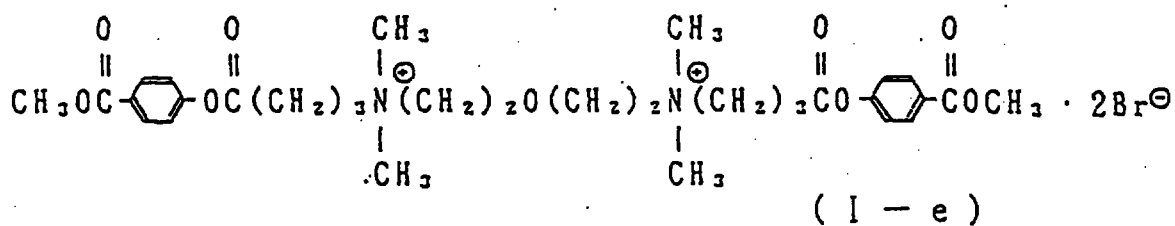
3034, 2950, 2830, 2782, 1773, 1722, 1635, 1608, 1488, 1467, 1437, 1281, 1227, 1164, 1134, 1110, 1059, 1011, 966, 927, 86

Example 5

synthesis of compound (I-e)

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The same procedure as in Example 1 was repeated except that 22.8 g of 2,2'-bis(N,N-dimethylamino)-diethyl ether (MW: 152.2, 0.15 mol) were used instead of the N,N,N',N'-tetramethylethylenediamine.
 amount: 59.4 g, purity: 80%, yield: 42%,
 MW: 754.8

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Example 6

synthesis of compound (I-f)

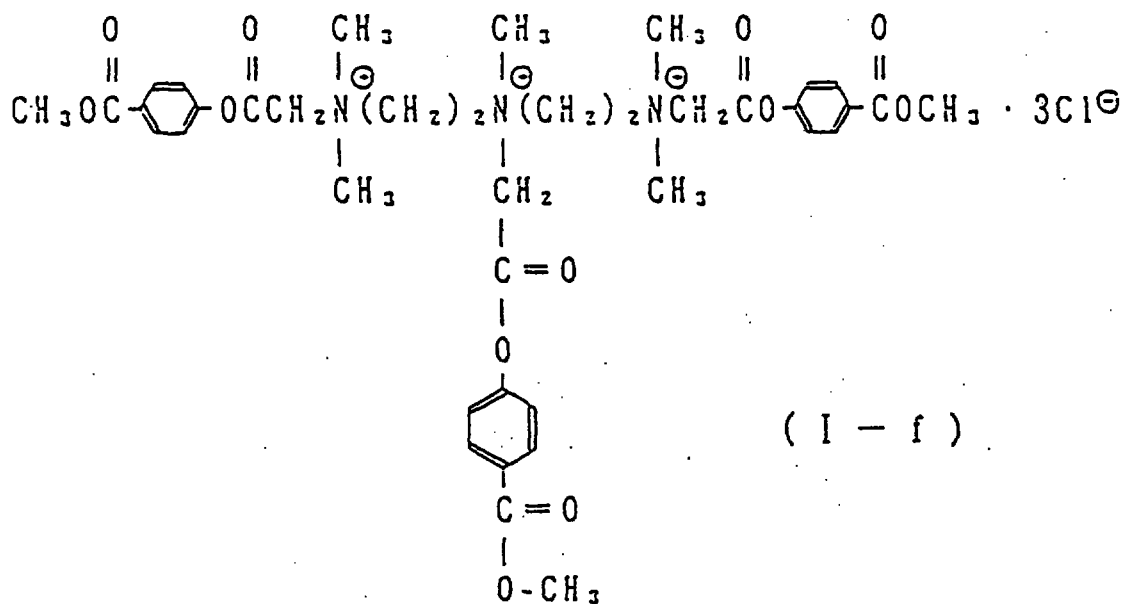
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The same procedure as in Example 3 was repeated except that 38.2 g of N,N,N',N'',N'''-diethylenetriamine (KAOLIZER No. 3, a product of Kao Corporation) (MW: 381.9, 0.10 mol) were used instead of the N,N,N',N'-tetramethylhexamethylenediamine.

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amount: 41.6 g, purity: 77%, yield: 30%,
 MW: 1067.7

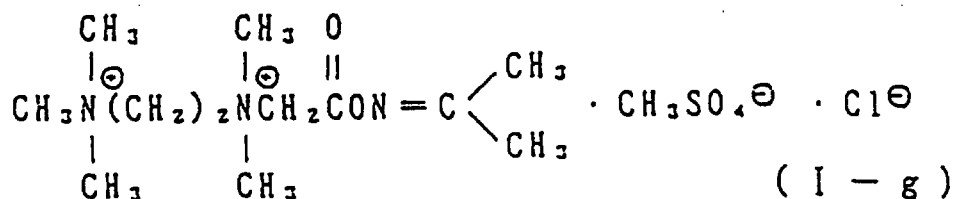
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Example 7

synthesis of compound (I-g)

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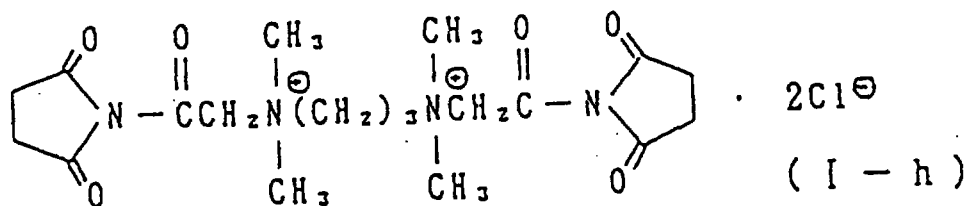
- 15 The same procedure as in Example 4 was repeated except that 22.4 g of the compound (3) (MW: 149.5, purity: 90%, 0.15 mol) were used instead of the compound (1).
 amount: 41.1 g, purity: 78%, yield: 55%,
 MW: 391.6

20 Example 8

synthesis of compound (I-h)

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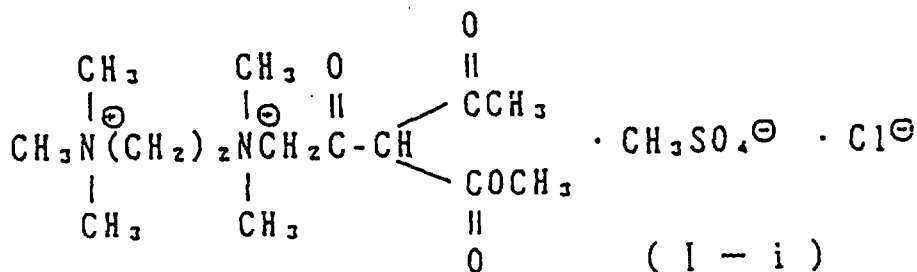
- 35 The same procedure as in Example 1 was repeated except that 62.5 g of the compound (4) (MW: 175.4, purity: 87%, 0.13 mol) and 19.5 g of N,N,N',N'-tetramethylpropylenediamine (MW: 130.23, 0.15 mol) were used instead of the compound (2).
 amount: 50.4 g, purity: 83%, yield: 53%,
 MW: 481.0

40 Example 9

synthesis of compound (I-i)

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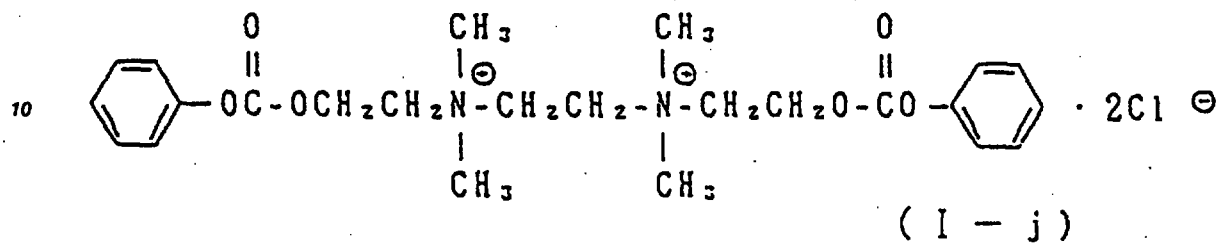
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- The same procedure as in Example 4 was repeated except that 44.7 g of the compound (5) (MW: 226.3, purity: 76%, 0.15 mol) were used instead of the compound (1).
 amount: 36.8 g, purity: 86%, yield: 45%,

MW: 468.4

Example 10

5 synthesis of compound (I-j)

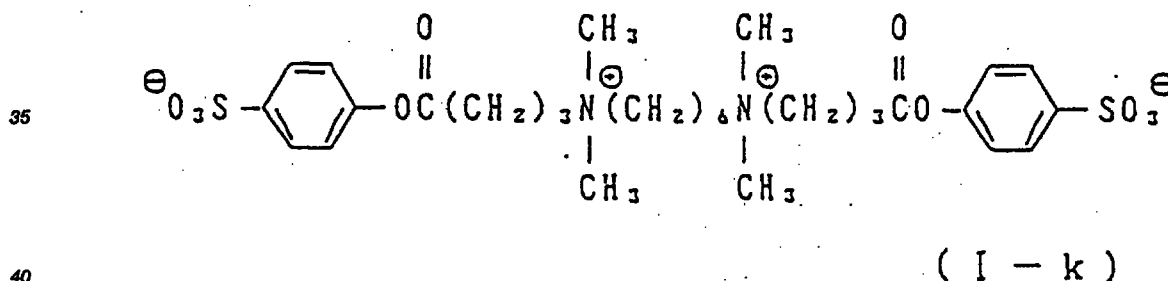


100 g (0.36 mol) of the compound (6), 57.0 g of pyridine (MW: 79.1, 0.72 mol) and 200 g of dimethylformamide were mixed together in a 1-l four-necked flask placed in an ice bath and fitted with a condenser, a thermometer, a mechanical stirrer and a dropping funnel. Thereafter, 112.8 g of phenyl chloroformate (MW: 156.6, 0.72 mol) were dropped into the flask through the dropping funnel over a period of about one hour. The reaction mixture was aged for 2 hours and distilled under a reduced pressure to remove the dimethylformamide. The residue was washed with THF several times to remove pyridine hydrochloride. The residue was recrystallized from acetonitrile to give 158.3 g of the compound (I-j).

25 MW: 517.2, purity: 95%, yield: 85%

Example 11

30 synthesis of compound (I-k)



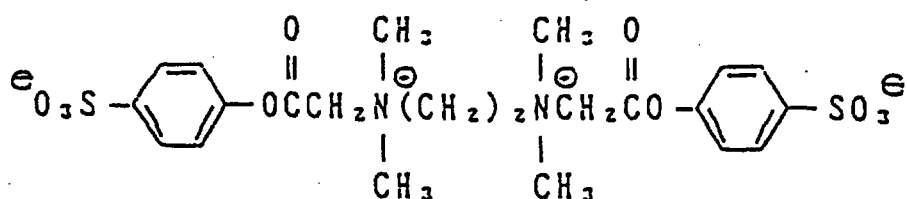
104.9 g (0.29 mol) of the compound (7), 300 g of N,N-dimethylformamide and 25.8 g of N,N,N',N'-tetramethylhexamethylenediamine (MW: 172, 0.15 mol) were mixed together in a 1-l four-necked flask fitted with a condenser, a mechanical stirrer, a thermometer and a dropping funnel and kept at 120 °C for about 12 hours to carry out a reaction. The disappearance of the compound (7) used as the starting material was confirmed by high-performance liquid chromatography. Thereafter, the reaction mixture was distilled under a reduced pressure to remove the N,N-dimethylformamide. The obtained solid was washed with acetone several times and dried to give 69.6 g of the compound (I-k).

50 MW: 656.2, purity: 82%, yield: 58%

55

Example 12

synthesis of compound (I-l)



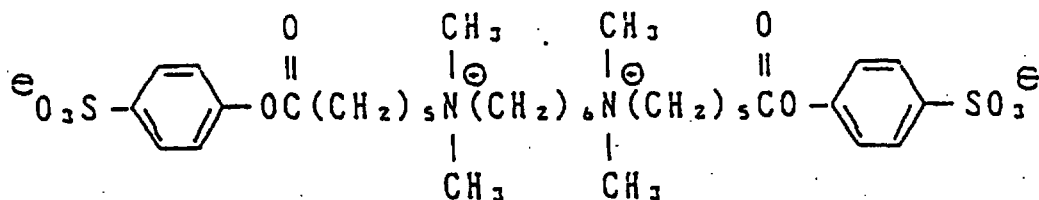
(I - l)

100 g (0.29 mol) of the compound (8), 300 g of N,N-dimethylformamide and 16.9 g of N,N,N',N'-tetramethylethylenediamine (MW: 116, 0.15 mol) were mixed together in a 1-l four-necked flask fitted with a condenser, a mechanical stirrer, a thermometer and a dropping funnel and kept at 80°C for about 5 hours to carry out a reaction. The disappearance of the compound (8) used as the starting material was confirmed by high-performance liquid chromatography. Thereafter, the reaction mixture was distilled under a reduced pressure to remove the N,N-dimethylformamide. The obtained solid was washed with acetone several times and dried to give 65.3 g of the compound (I-l).

MW: 544.2, purity: 80%, yield: 64%

Example 13

synthesis of compound (I-m)



(I - m)

108.2 g (0.29 mol) of the compound (9), 324.6 g of N,N-dimethylformamide and 24.9 g of N,N,N',N'-tetramethylhexamethylenediamine (MW: 172, 0.145 mol) were mixed together in a 1-l four-necked flask fitted with a condenser, a mechanical stirrer, a thermometer and a dropping funnel and kept at 60°C for about 2 hours to carry out a reaction. The disappearance of the compound (9) used as starting material was confirmed by high-performance liquid chromatography. Thereafter, the reaction mixture was distilled under a reduced pressure to remove the N,N-dimethylformamide. The obtained solid was washed with acetone several times and dried to give 81.9 g of the compound (I-m).

MW: 712.6, purity: 82%, yield: 65%

(Test Example)

Determination of bleaching effect

Sodium percarbonate was dissolved in 300 ml of water at 20°C so as to give an effective oxygen content of 0.05%. The compounds (I-a) to (I-m) and tetraacetythylenediamine (TAED) for comparison were

each added to the obtained solution in an amount as specified in Table 1 to give an equivalent ratio of the compound to the hydrogen peroxide contained in the solution of 1/6. Five tea-stained cloths*prepared by the method which will be described below were dipped in the solution prepared above for 30 minutes, washed with water and dried. The rate of bleaching of the resulting cloth was determined according to the following

equation:

rate of bleaching of tea-stained cloth:

rate of bleaching (%) =

$$\frac{(\text{reflectance after bleaching}) - (\text{reflectance before bleaching})}{(\text{reflectance of white cloth}) - (\text{reflectance before bleaching})} \times 100$$

The reflectance was determined with an NDR-1001 DP (mfd. by Nippon Denshoku Kogyo) with a filter of 460 nm. The larger the value, the higher the rate of bleaching.

*tea-stained cloth:

80 g of Nitto black teat yellow package) were dipped in 3 l of ion-exchanged water, boiled for about 15 minutes, and filtered through a desired bleached cotton cloth. A cotton shirting cloth #2003 was dipped in the obtained filtrate, followed by boiling for about 15 minutes. The boiled liquid was taken off the fire and allowed to stand for about 2 hours. The cloth was dried spontaneously, washed with water until the washings became colorless, dehydrated, pressed and cut into a test piece of 8 cm x 8 cm. This test piece was used in the above determination.

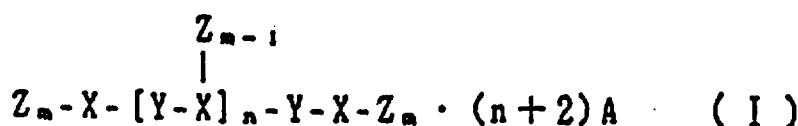
The results are given in Table 1.

Table 1

bleaching activator (wt.%)	Invention													Comp.	
	1	2	3	4	5	6	7	8	9	10	11	12	13	1	2
sodium percarbonate	82	80	84	78	80	80	79	87	77	88	85	87	84	94	100
I - a	18														
I - b		20													
I - c			16												
I - d				22											
I - e					20										
I - f						20									
I - g							21								
I - h								13							
I - i									23						
I - j										12					
I - k											15				
I - l												13			
I - m													16		
T A E D														6	
rate of bleaching (%)	40	40	42	41	40	42	40	41	40	40	42	41	43	23	15

Claims

1. A polycationic compound having the formula (I):

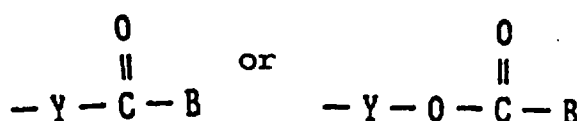


wherein

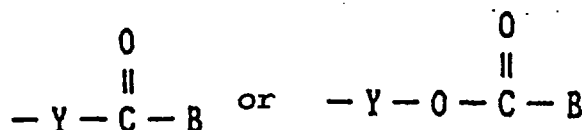
X: an N^+ cationic group,

Y: an alkylene group having 1 to 9 carbon atoms, which may be substituted with a hydroxyl group or a $-(C_2H_4O)_{1-5}-C_2H_4-$ or $-(C_3H_6O)_{1-5}-C_3H_6-$ group, wherein a plurality of Y groups may be the same or different from each other,

Z: an



group (wherein B will be defined below), an alkyl group having 1 to 20 carbon atoms or an alkenyl group, each of which may be substituted with a hydroxyl group, or a $-(C_2H_4O)_{1-5}-H$ or $-(C_3H_6O)_{1-5}-H$ group, with the proviso that at least one Z group is a



group, though the Z groups may be the same or different from each other,

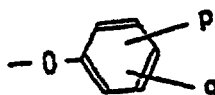
m: is 3 with respect to the Z_m or Z_{m-1} groups bonded to the X group,

n: a number of 0 to 3,

A: an inorganic or organic anionic group, with the proviso that A is absent when Z and X are combined together to form an inner salt, wherein a plurality of A groups may be the same or different from each other,

wherein a plurality of the above B groups represent each any of the following groups and may be the same or different from each other in one molecule:

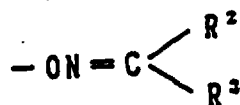
a)



(wherein p and q each represent $-H$, $-SO_3M$, $-COOM$, $-COOR^1$, a halogen atom, $-OR^1$, or $-N(R^1)_3$ • A, wherein M represents an alkali metal, an alkaline earth metal, an ammonium, an alkanolammonium or a negative charge necessary to build the inner salt, R^1 represents an alkyl group having 1 to 20 carbon atoms, an alkenyl or hydroxyalkyl group or a $-(C_2H_4O)_{1-5}-H$ or $-(C_3H_6O)_{1-5}-H$ group; A is as defined above and p and q may be the same or different from each other),

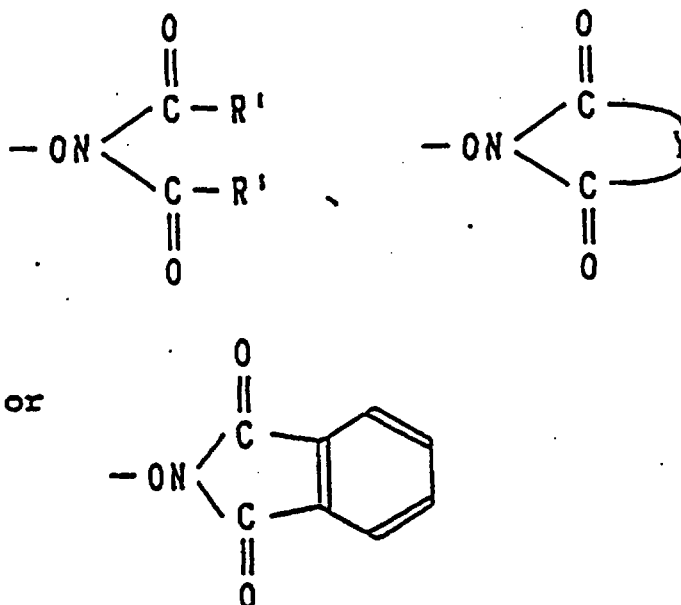


b) an oxime group having a structure represented by the formula



(wherein R^2 and R^3 are the same as those defined above with respect to R^1 and may be the same or different from each other, with the proviso that at least one of R^2 and R^3 must not be H),

c) an imidoxime group represented by the formula:



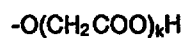
(wherein R^1 and Y are as defined above),

d) an alkanesulfonic acid group represented by the formula:



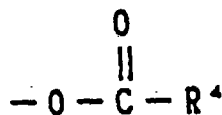
(wherein Y and M are as defined above),

e) a polyglycolic ester group represented by the formula:



(wherein k is a number of 1 to 10),

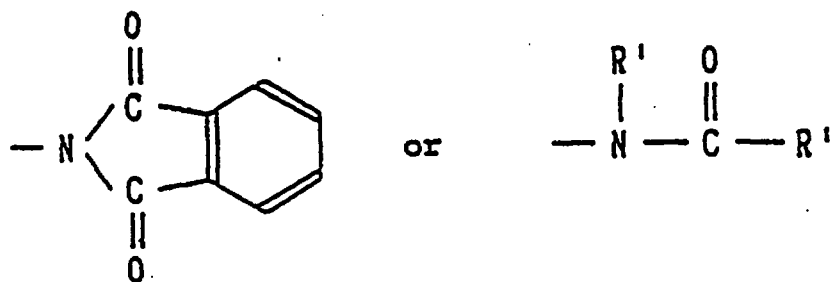
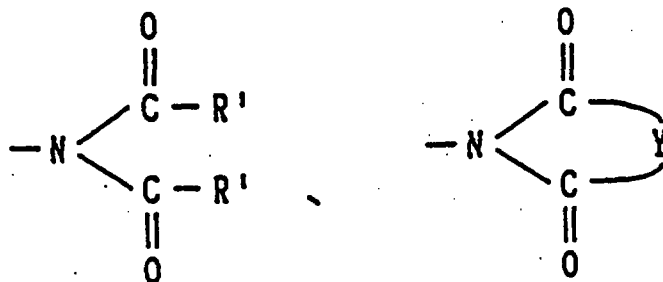
f) an acid anhydride group represented by the formula:



(wherein R^4 represents an alkyl group having 1 to 22 carbon atoms, an alkenyl group or a phenyl group which may be substituted),

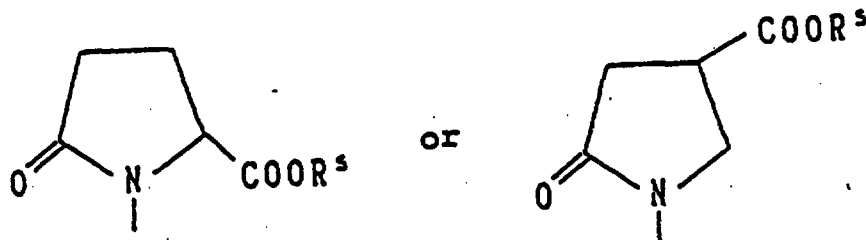


g) an imide group represented by the formula:



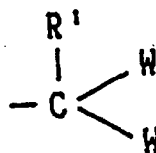
(wherein R^1 and Y are as defined above)

h) a pyrrolidonecarboxylic acid derivative group represented by the formula:



(wherein R^5 is the same as that defined above with respect to R^1 or M),

i) a ketone derivative represented by the formula:



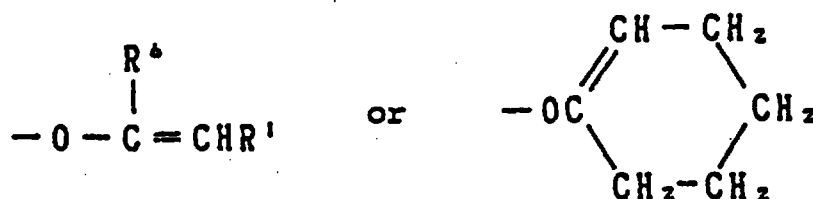
(wherein R^1 is as defined above and W is



$-\text{C}=\text{N},$



-NO₂ or -SO₂R¹, wherein a plurality of W groups may be the same or different from each other),
or
j) an enol derivative group represented by the formula:

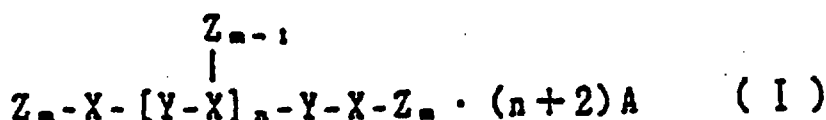


(wherein R⁶ is the same as that defined above with respect to R¹ excepting H).

2. A bleach composition comprising a peroxide and the polycationic compound as set forth in claim 1 as an organic peracid precursor.
3. A bleach composition as set forth in claim 2, wherein said peroxide is hydrogen peroxide or a peroxide which can generate hydrogen peroxide in an aqueous solution.

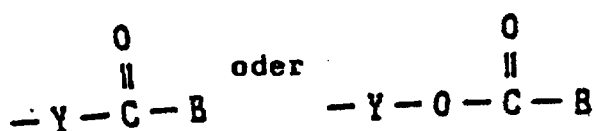
Patentansprüche

1. Polykationische Verbindung der Formel (I):

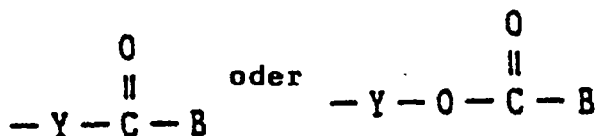


worin bedeuten:

- X: eine kationische N⁺-Gruppe,
Y: eine Alkylengruppe mit 1 bis 9 Kohlenstoffatomen, welche mit einer Hydroxylgruppe oder einer -(C₂H₄O)₁₋₅-C₂H₄- oder -(C₃H₅O)₁₋₅-C₃H₅-Gruppe substituiert sein kann, wobei eine Vielzahl von Y-Gruppen gleich oder verschieden sein kann,
Z: eine



Gruppe, (wobei B nachfolgend definiert wird), eine Alkylgruppe mit 1 bis 2 Kohlenstoffatomen oder eine Alkenylgruppe, wobei jede mit einer Hydroxylgruppe oder einer -(C₂H₄O)₁₋₅-H- oder -(C₃H₅O)₁₋₅-H-Gruppe substituiert sein kann, mit der Maßgabe, daß wenigstens eine Z-Gruppe eine



Gruppe ist, obgleich die Z-Gruppen gleich oder verschieden sein können,
m: 3, bezüglich der Z_m- oder Z_{m-1}-Gruppen, die an die X-Gruppe gebunden sind,
n: eine Zahl von 0 bis 3,



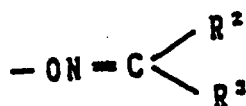
A: eine anorganische oder organische anionische Gruppe, mit der Maßgabe, daß A nicht vorhanden ist, falls Z und X zur Bildung eines inneren Salzes miteinander kombiniert werden, wobei eine Vielzahl von A-Gruppen gleich oder verschieden sein können, wobei eine Vielzahl der obigen B-Gruppen jeweils irgendeine der folgenden Gruppen repräsentieren und gleich oder verschieden in einem Molekül sein können:

a)



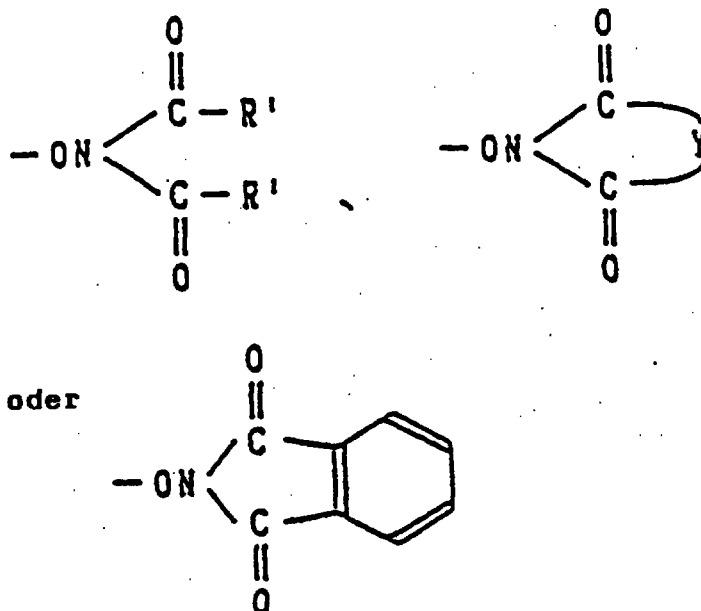
(worin p und q jeweils -H, -SO₃M, -COOM, -COOR¹, ein Halogenatom, -OR¹ oder -N(R¹)₃ • A bedeuten, wobei M ein Alkalimetall, ein Erdalkalimetall, ein Ammonium, ein Alkanolammonium oder eine negative Ladung, die notwendig ist zur Ausbildung des inneren Salzes, repräsentiert, R¹ steht für eine Alkylgruppe mit 1 bis 20 Kohlenstoffatomen, eine Alkenyl- oder Hydroxyalkylgruppe oder eine -(C₂H₄O)₁₋₅-H- oder -(C₃H₆O)₁₋₅-H-Gruppe; A besitzt die oben definierte Bedeutung und p und q können gleich oder verschieden sein),

b) eine Oximgruppe mit einer durch die Formel



dargestellten Struktur (wobei R² und R³ die gleiche Bedeutung wie oben definiert besitzen bezüglich R¹ und gleich oder verschieden sein können, mit der Maßgabe, daß wenigstens eines von R² und R³ nicht H sein muß),

c) eine Imidoximgruppe, repräsentiert durch die Formel:



(worin R¹ und Y wie oben definiert sind),

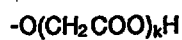
d) eine Alkansulfonsäuregruppe, repräsentiert durch die Formel:



(worin Y und M wie oben definiert sind),

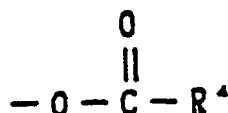


e) eine Polyglykolestergruppe, repräsentiert durch die Formel:



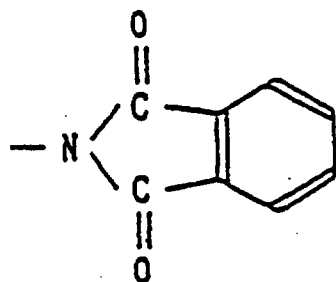
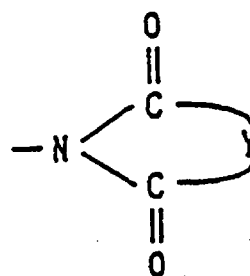
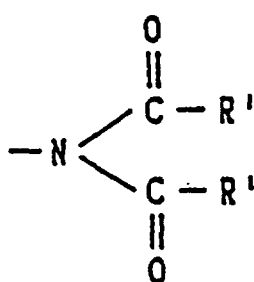
(worin k eine Zahl von 1 bis 10 ist),

f) eine Säureanhydridgruppe, repräsentiert durch die Formel:

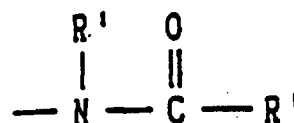


(worin R⁴ für eine Alkylgruppe mit 1 bis 22 Kohlenstoffatomen, eine Alkenylgruppe oder eine Phenylgruppe steht, die substituiert sein können),

g) eine Imidgruppe, repräsentiert durch Formel:

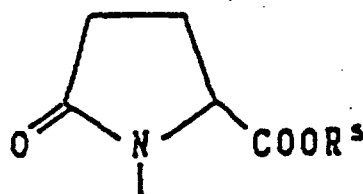


oder

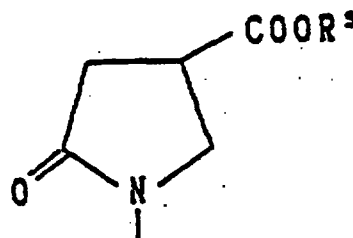


(worin R¹ und Y wie oben definiert sind),

h) eine Pyrrolidoncarbonsäurederivatgruppe, repräsentiert durch die Formel:



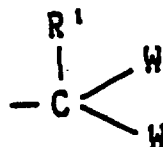
oder



(worin R⁵ gleich ist wie oben definiert bezüglich R¹ oder M),



i) eine Ketonderivatgruppe, repräsentiert durch die Formel:



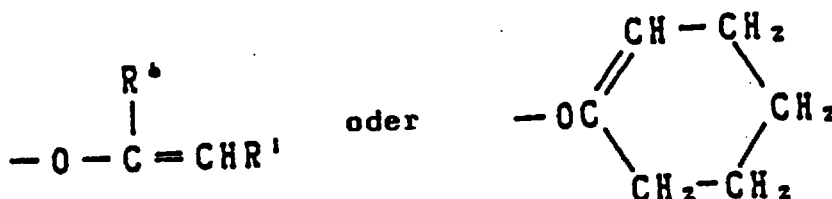
(worin R¹ wie oben definiert ist und W



-C=N,

-NO₂ oder oder -SO₂R¹ bedeutet, worin eine Vielzahl von W-Gruppen gleich oder verschieden sein können), oder

j) eine Enolderivatgruppe, repräsentiert durch die Formel:



(worin R⁶ gleich ist wie oben definiert bezüglich R¹ mit der Ausnahme von H).

2. Bleichzusammensetzung, umfassend ein Peroxid und die polykationische Verbindung gemäß Anspruch 1 als organischen Persäurevorläufer.
3. Bleichzusammensetzung nach Anspruch 2, worin das Peroxid Wasserstoffperoxid oder ein Peroxid ist, welches Wasserstoffperoxid in wäßriger Lösung erzeugen kann.

Revendications

1. Composé polycationique ayant la formule (I):



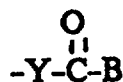
dans laquelle

X : est un groupe cationique N⁺,

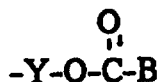
Y : est un groupe alkylène ayant de 1 à 9 atomes de carbone, qui peut être substitué par un groupe hydroxyle, ou un groupe -(C₂H₄O)₁₋₅-C₂H₄- ou -(C₃H₆O)₁₋₅-C₃H₆-, où une pluralité de groupes Y peuvent être les mêmes ou différents entre eux,

Z : est un groupe

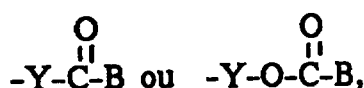




ou un groupe



(où B sera défini ci-après), un groupe alkyle ayant de 1 à 20 atomes de carbone ou un groupe alcényle, dont chacun peut être substitué par un groupe hydroxyle, ou un groupe $-(\text{C}_2\text{H}_4\text{O})_1-5-\text{H}$ ou $-(\text{C}_3\text{H}_5\text{O})_1-5-\text{H}$, une condition à satisfaire étant qu'au moins un groupe Z soit un groupe



étant entendu que les groupes Z peuvent être identiques ou différents entre eux,

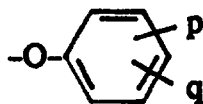
m : est égal à 3 dans les groupes Z_m et Z_{m-1} liés au groupe X,

n : est un nombre entre 0 et 3,

A : est un groupe anionique minéral ou organique, une condition à satisfaire étant que A soit absent lorsque Z et X sont combinés ensemble pour former un sel interne, où une pluralité de groupes A peuvent être identiques ou différents entre eux,

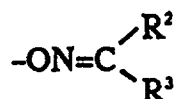
dans laquelle chaque groupe de la pluralité de groupes B ci-dessus représente un quelconque des groupes suivants, ces groupes étant identiques ou différents entre eux dans une molécule :

a)



(où p et q représentent chacun $-\text{H}$, $-\text{SO}_3\text{M}$, $-\text{COOM}$, $-\text{COOR}^1$, un atome d'halogène, $-\text{OR}^1$ ou $-\text{N}(\text{R}^1)-3.\text{A}$, où M représente un métal alcalin, un métal alcalino-terreux, un ammonium, un alcanolammonium ou une charge négative nécessaire pour former un sel interne, R^1 représente un groupe alkyle ayant de 1 à 20 atomes de carbone, un groupe alcényle, un groupe hydroxyalkyle ou un groupe $-(\text{C}_2\text{H}_4\text{O})_1-5-\text{H}$ ou $-(\text{C}_3\text{H}_5\text{O})_1-5-\text{H}$; A est comme défini ci-dessus, et p et q peuvent être identiques ou différents entre eux),

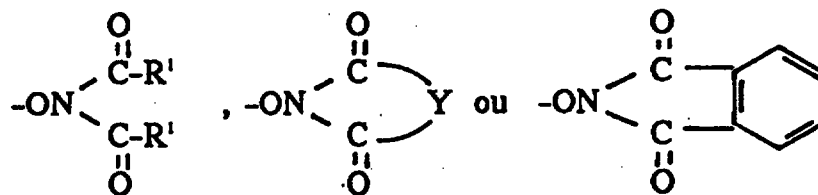
b) un groupe oxime ayant une structure représentée par la formule



(où R^2 et R^3 ont la même définition que celle donnée ci-dessus pour R^1 et ils peuvent être identiques ou différents entre eux, une condition à satisfaire étant toutefois qu'au moins un d'entre R^2 et R^3 ne doit pas être H).



c) un groupe imidoxime représenté par la formule :



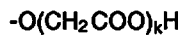
(où R^1 et Y sont comme défini ci-dessus),

d) un groupe acide alcane sulfonique représenté par la formule :



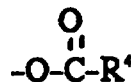
(où Y et M sont comme défini ci-dessus),

e) un groupe ester polyglycolique représenté par la formule :



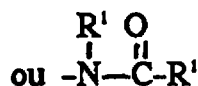
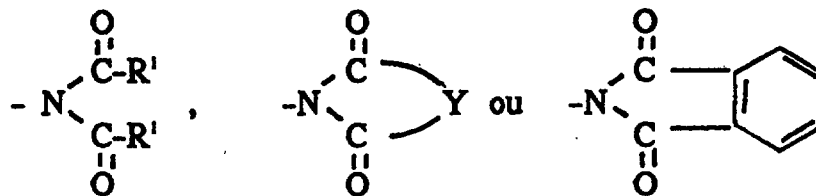
(où k est un nombre situé entre 1 et 10),

f) un groupe anhydride d'acide représenté par la formule :



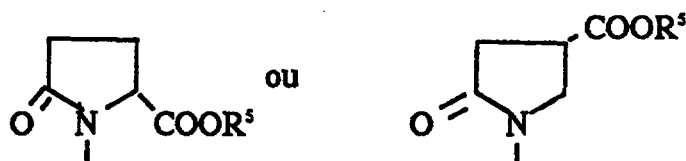
(où R^4 représente un groupe alkyle ayant de 1 à 22 atomes de carbone, un groupe alcényle ou un groupe phényle qui peut être substitué),

g) un groupe imide représenté par la formule :



(où R^1 et Y sont comme défini ci-dessus)

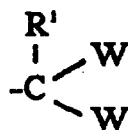
h) un groupe dérivé de l'acide pyrrolidonecarboxylique représenté par la formule



(où la définition de R^5 est identique à celle donnée ci-dessus pour R^1 ou M),



i) un groupe dérivé d'une cétone représenté par la formule :



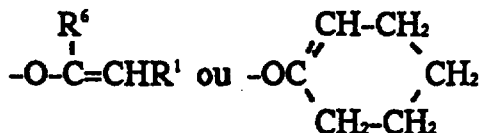
(où R' est comme défini ci-dessus et W est



-C=N, -NO₂ ou -SO₂R', où une pluralité de groupes W peuvent être identiques ou différents entre eux),

ou

j) un groupe dérivé d'un énoI représenté par la formule



(où la définition de R⁵ est identique à celle donnée ci-dessus pour R', exception faite de H).

2. Composition de blanchiment contenant un peroxyde et le composé polycationique comme décrit dans la revendication 1, servant de précurseur de peracide organique.
3. Composition de blanchiment selon la revendication 2, où ledit peroxyde est le peroxyde d'hydrogène ou un peroxyde qui peut produire du peroxyde d'hydrogène dans une solution aqueuse.

