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(72) Kawashima, Mitsunobu, JP
(72) Omura, Ikuo, JP
(73) Kuraray Co., Ltd., JP
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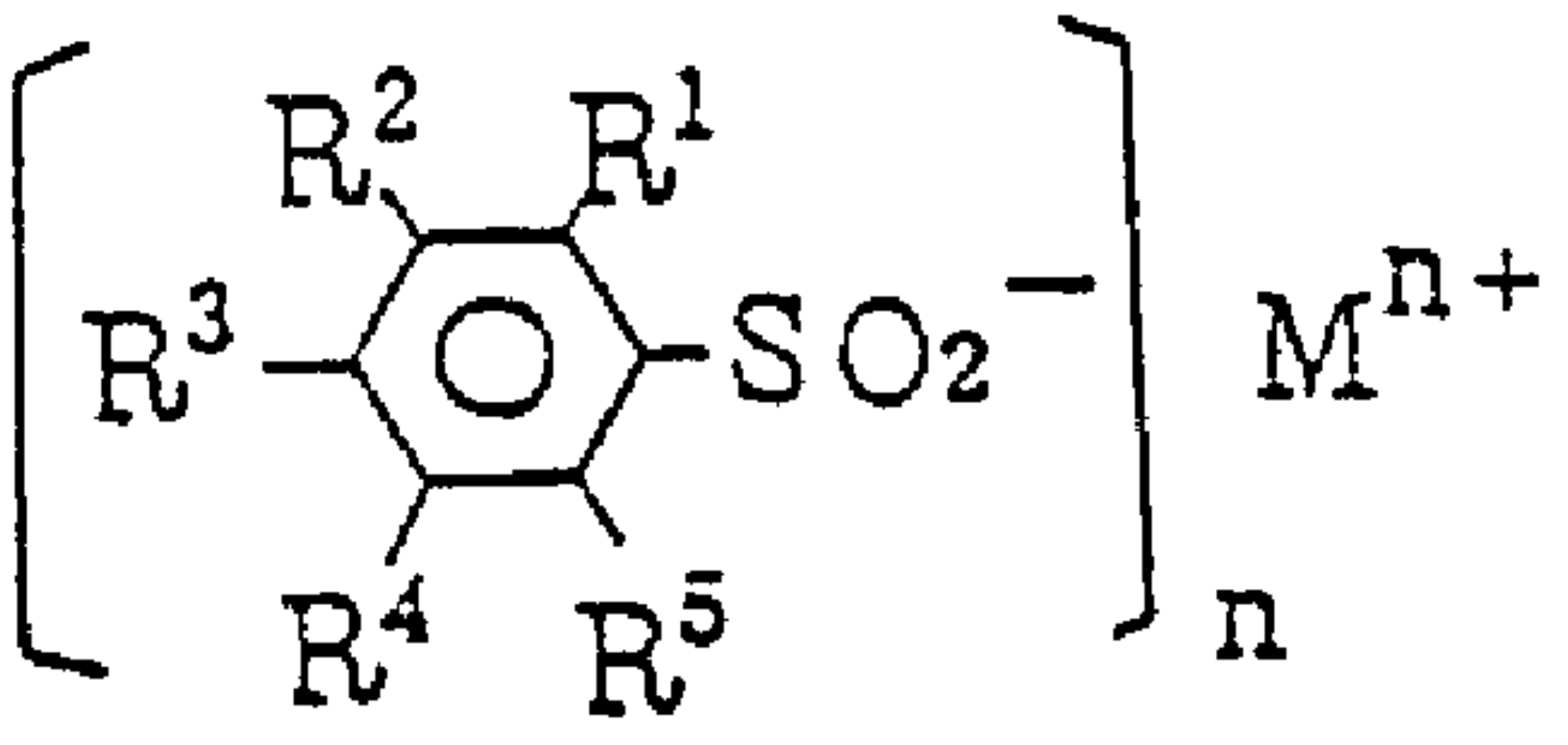
(54) **COMPOSITIONS POLYMERISABLES**
(54) **POLYMERIZABLE COMPOSITIONS**



[I]

(57) Provided are polymerizable compositions comprising: (a) a sulfinate represented by the general formula (I) (see formula I) wherein R^1 and R^5 each represents a substituent having 2 to 6 carbon atoms, R^2, R^3 and R^4 each represents an atom or substituent inert to the below-described monomer (b), M^{n+} represents a n-valent cation and n represents an integer of 1 to 4; and (b) a monomer. (a) is an aromatic sulfinate substituted with bulky groups at its positions 2 and 6. Since the bulky substituents dramatically suppress the addition of the sulfinate to the double bond of the monomers, e.g. (meth)acrylates, (meth)acrylamides and derivatives thereof, the compositions can be stored at room temperature for at least 1 year and thus are of great industrial value and, in particular very useful as dental adhesive compositions.

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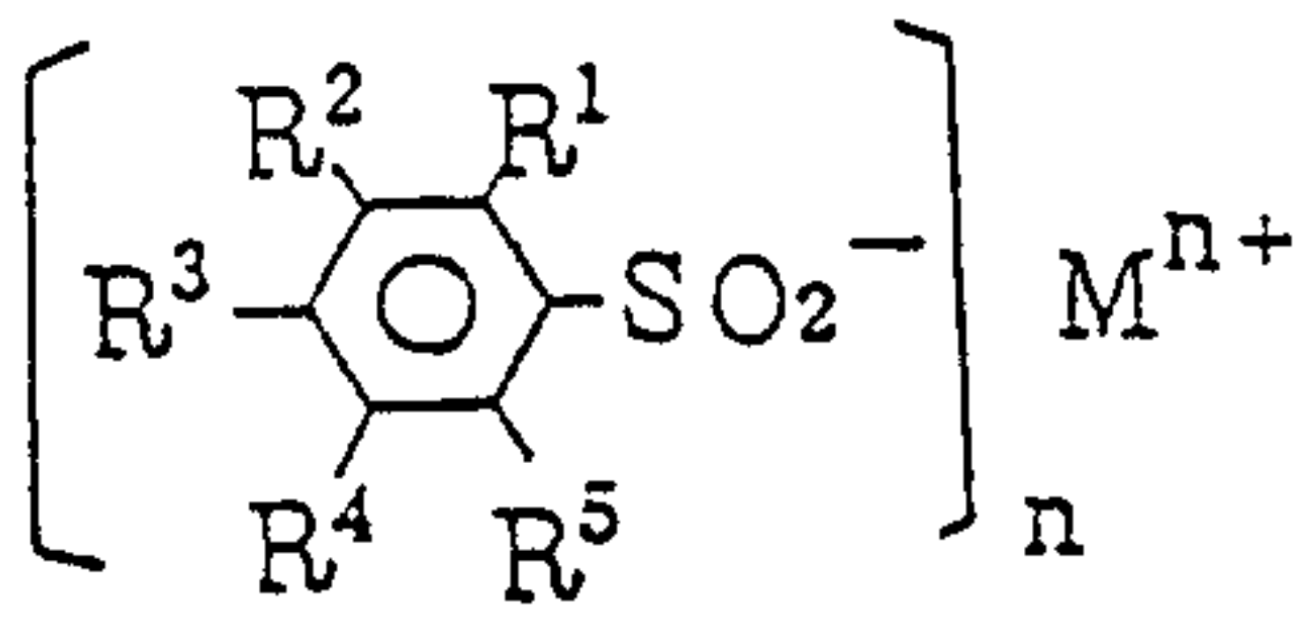
ABSTRACT OF THE DISCLOSURE

Provided are polymerizable compositions comprising:

(a) a sulfinate represented by the general formula [I]



[I]

wherein R^1 and R^5 each represents a substituent having 2 to 6 carbon atoms, R^2, R^3 and R^4 each represents an atom or substituent inert to the below-described monomer (b), M^{n+} represents a n-valent cation and n represents an integer of 1 to 4; and

(b) a monomer.

(a) is an aromatic sulfinate substituted with bulky groups at its positions 2 and 6. Since the bulky substituents dramatically suppress the addition of the sulfinate to the double bond of the monomers, e.g. (meth)acrylates, (meth)acrylamides and derivatives thereof, the compositions can be stored at room temperature for at least 1 year and thus are of great industrial value and, in particular very useful as dental adhesive compositions.

POLYMERIZABLE COMPOSITION

BACKGROUND OF THE INVENTION

Field of the invention

The present invention relates to polymerizable compositions, and more specifically to polymerizable compositions with excellent storage stability comprising an aromatic sulfinate as polymerization initiator.

Description of prior art

There is known as a means for polymerizing radical-polymerizable monomers the use of a sulfinic acid or its salt, such as sulfinic acids, sulfinic acid or its salt-oxidizer system, and sulfinic acid or its salt-amine-peroxide system, as a component of polymerization initiator. For example Japanese Patent Application Laid-open No. 30193/1978 discloses a process comprising the use of a sulfinate-amine-peroxide system as a polymerization initiator for radical-polymerizable monomers. Further Japanese Patent Application Laid-open No. 75907/1982 discloses that this sulfinate-amine-peroxide system is particularly useful for the polymerization of dental adhesives comprising an acidic monomer.

However, since aromatic sulfinates which have hitherto been used, e.g. benzenesulfinate and toluenesulfinate, add, when contacted with a (meth)acrylate, (meth)acrylamide or (meth)acrylamide derivative, gradually to the double bond of the monomer, compositions comprising the sulfinate dissolved or suspended in the monomer will, when stored at a room temperature, lose the polymerization activity in a few weeks.

The two components therefore must be stored in separate packages so that they will not be in contact with each other, which is a disadvantage in comparison with other systems that can be packed and stored together with its initiator and monomer.

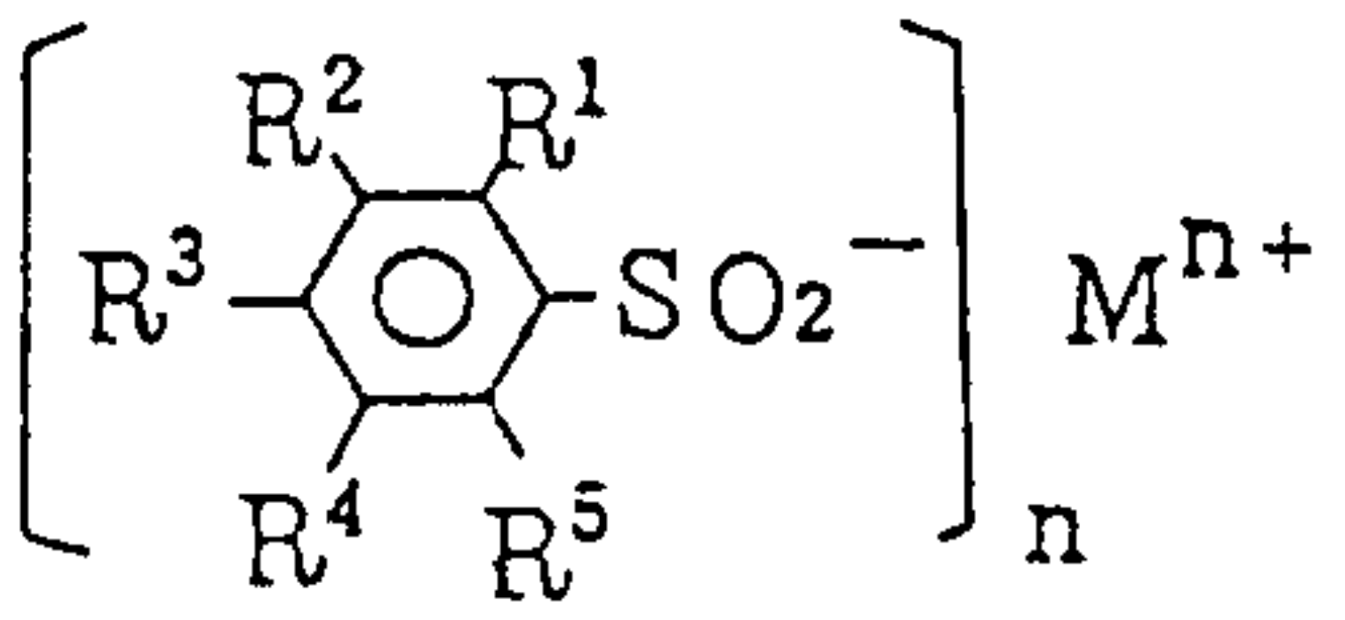
SUMMARY OF THE INVENTION

Accordingly, an object of the present invenion is to provide a composition comprising a sulfinate and a monomer, which has a pot life of at least one year and comprising a sulfinate and a polymerizable monomer.

As a result of an intensive study to solve the above problem, we found that introduction of bulky substituents into positions 2 and 6 of aromatic sulfinates dramatically suppress the addition of these sulfinates to the double bond of (meth)acrylates, (meth)acrylamides or derivatives thereof.

Thus, the present invention provides a composition comprising:

(a) a sulfinate initiator component represented by the general formula [I]



[I]

wherein R^1 and R^5 each represents a substituent having 2 to

6 carbon atoms, R^2, R^3 and R^4 each represents an atom or substituent inert to the below-described monomer (b), M^{n+} represents a n-valent cation, and n represents an integer of 1 to 4; and

(b) a monomer having at least one polymerizable carbon-carbon double bond.

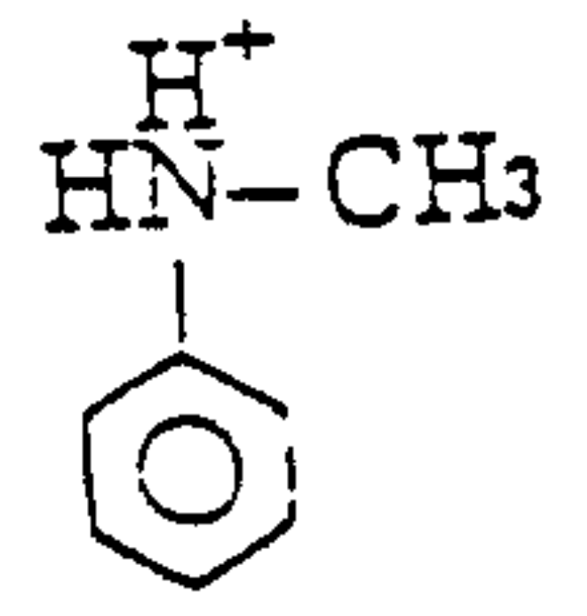
DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

The present invention is characterized by the use of aromatic sulfinates represented by the general formula [I] having bulky substituents in their positions 2 and 6.

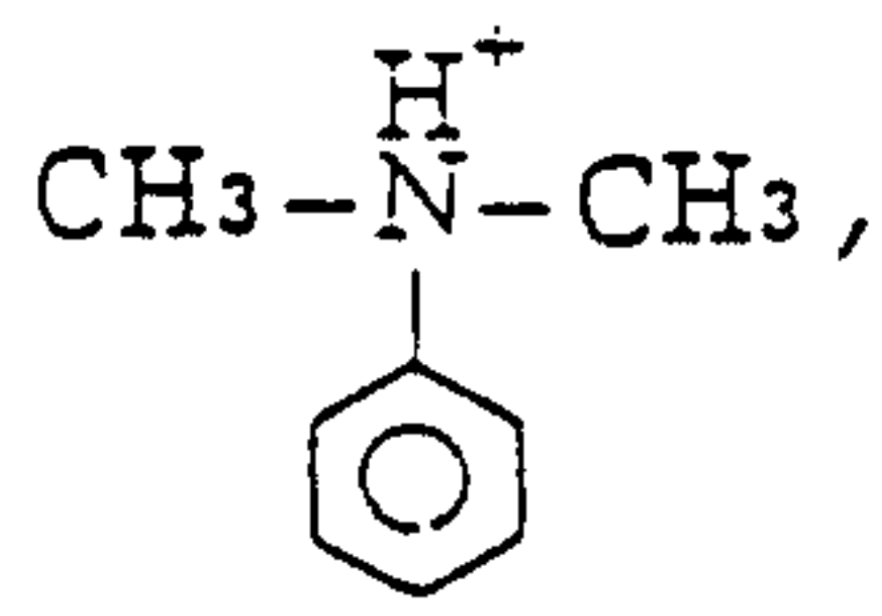
In the above-mentioned general formula [I], R^1 and R^5 each is a substituent located in the ortho-position to the sulfinate group of the aromatic sulfinate and having sufficient bulkiness for exerting steric hindrance to addition of the sulfinate group to carbon-to-carbon double bond of a monomer. It is important that both R^1 and R^5 be bulky groups. If only one of the two groups is bulky, sufficient steric hindrance to the addition of the sulfinate group to the double bond will not be exerted to achieve the object of the present invention. With respect to the bulkiness of the groups, although a carbon atom number of 1, i.e. methyl group, may suppress the addition reaction, practical level of the effect is attained with the carbon atom number of at least 2, particularly at least 3. While the addition is suppressed to a larger extent with increasing number of carbon atoms, the effect of the suppression will become smaller once the substituent has a bulkiness of a certain degree. In view of this and commercial availability of raw material, the number of carbon atoms is upto 6 for practical purposes. R^1 and R^5 should, naturally, be inert to the double bond of monomers. Thus, R^1 and R^5 each is a hydrocarbon group which has 2 to 6 carbon atoms and may be substituted with one or more halogen atoms. Examples of the group are ethyl, 2-chloroethyl, 2-bromo-2-chloroethyl, propyl, isopropyl, perfluoropropyl, allyl, butyl, isobutyl, sec-butyl, tert-butyl, pentyl, isopentyl, neopentyl, tert-pentyl, cyclohexyl, phenyl, 4-bromophenyl and the like.

R^2, R^3 and R^4 may be any atoms and/or groups as long as they are inert to the double bond of monomers. Their examples are hydrogen, fluoro, chloro, bromo, iodo, methyl, ethyl, 2-chloroethyl, 2-bromo-2-chloroethyl, propyl, isopropyl, per-fluoropropyl, allyl, butyl, isobutyl, sec-butyl, tert-butyl, pentyl, isopentyl, neopentyl, tert-pentyl, cyclohexyl, phenyl and 4-bromophenyl.

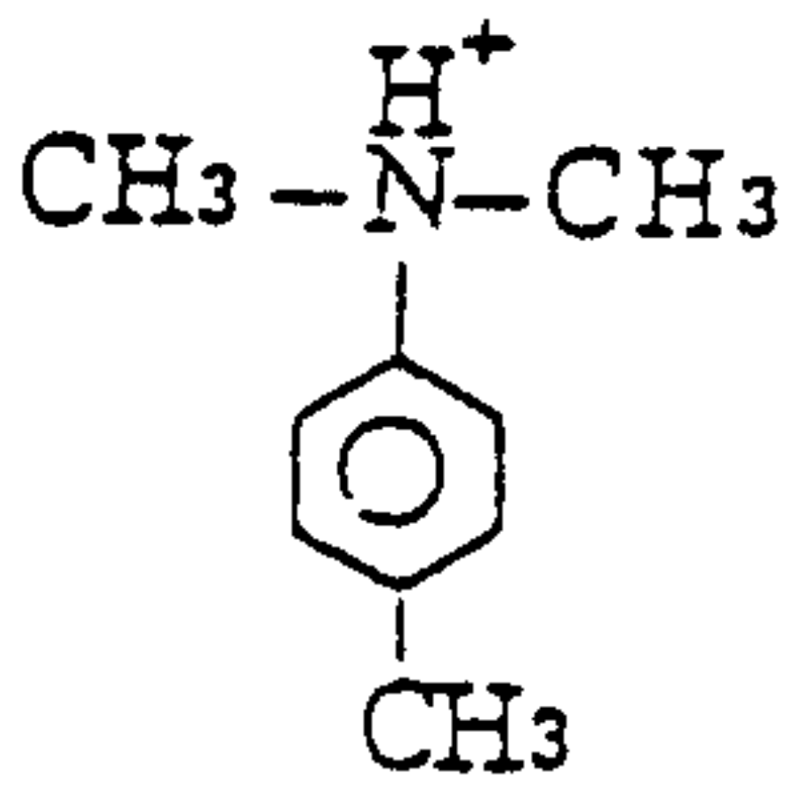
M^{n+} is a cation with monovalency to 4 valency that can, as a counter ion for a sulfinic acid anion, form the sulfinate. Examples of M^{n+} are alkali metal ions, such as Li^+, Na^+, K^+, Rb^+ and Cs^+, alkali earth metal ions, such as Be^{2+}, Mg^{2+}, Ca^{2+}, Sr^{2+} and Ba^2, transition metal ions, such as Cr^{2+}, Cr^{3+}, Mn^{2+}, Fe^{2+}, Fe^{3+}, Co^{2+}, CO^{3+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Rh^{3+}, Pd^{2+}, Ag^+, Cd^{2+}, Ir^{3+}, Ir^{4+} and Hg^{2+}, and ammonium ions, such as NH_4^+, $(CH_3CH_2)_3NH^+$,



$\overset{H^{+}}{HN}-CH_3$,



$CH_3-\overset{H^{+}}{N}-CH_3$,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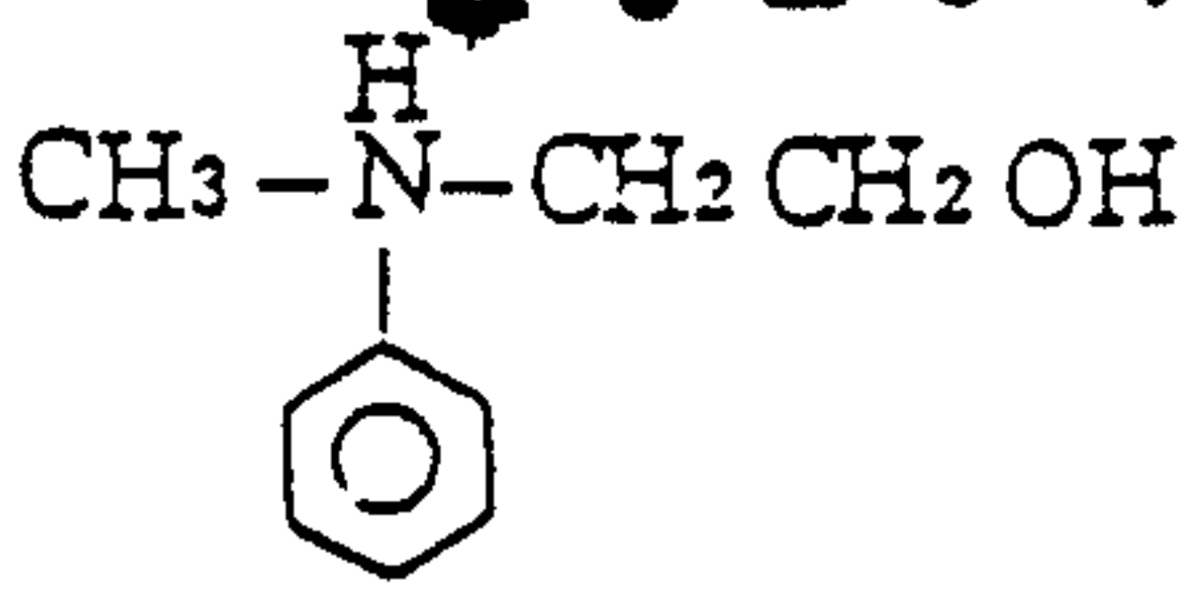
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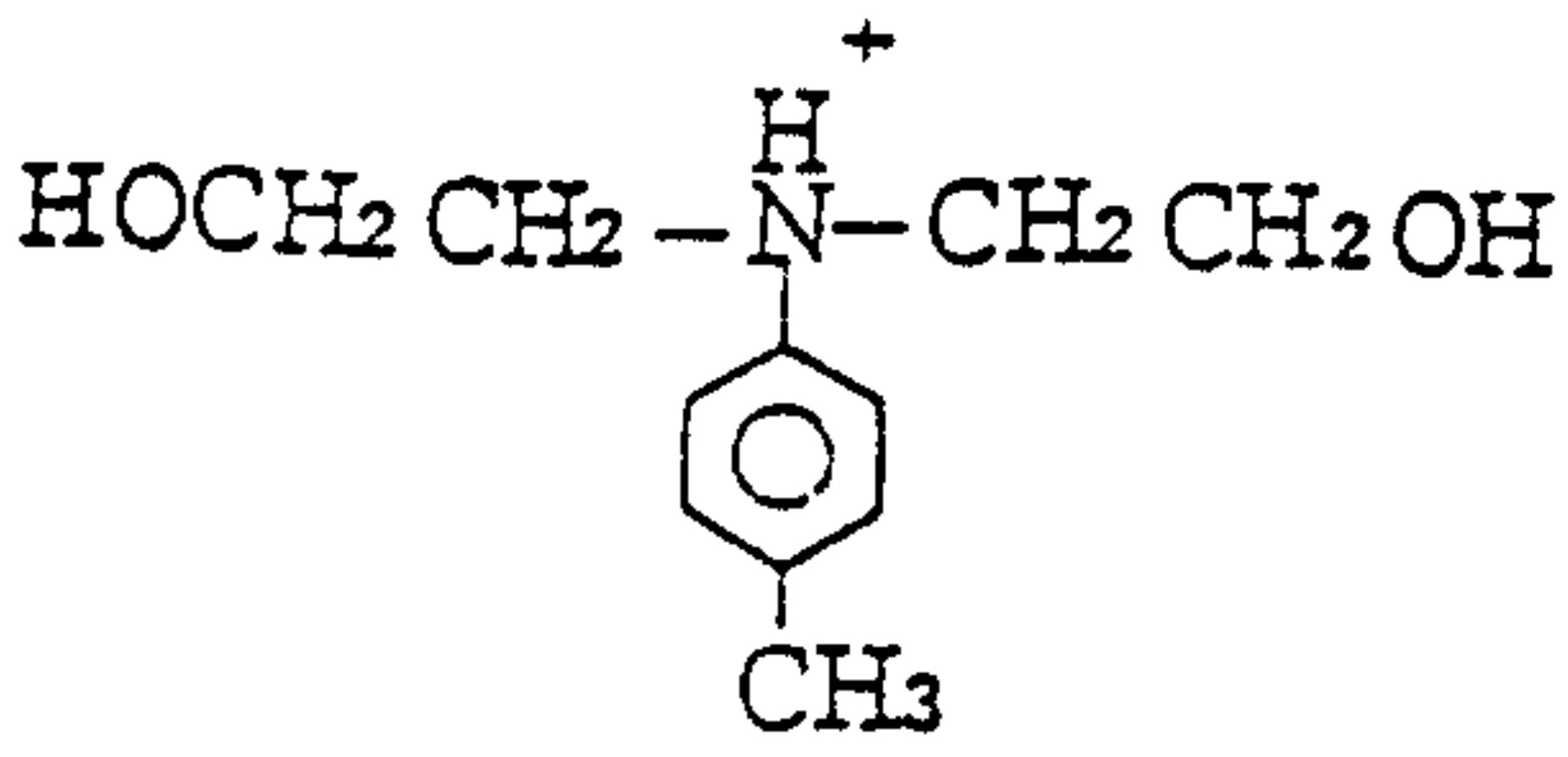
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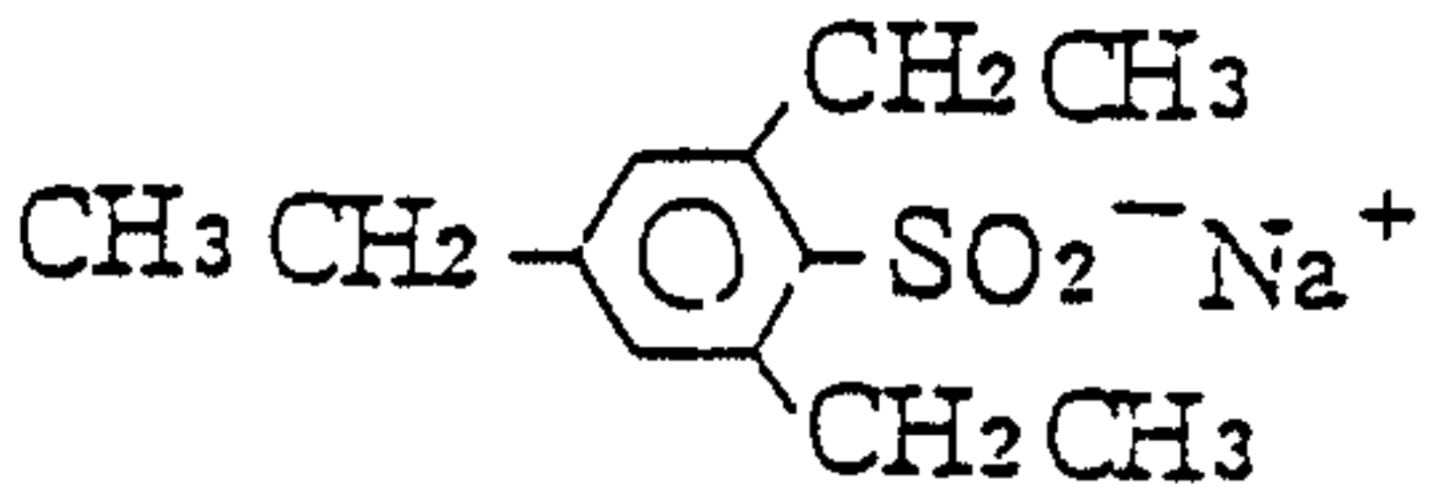
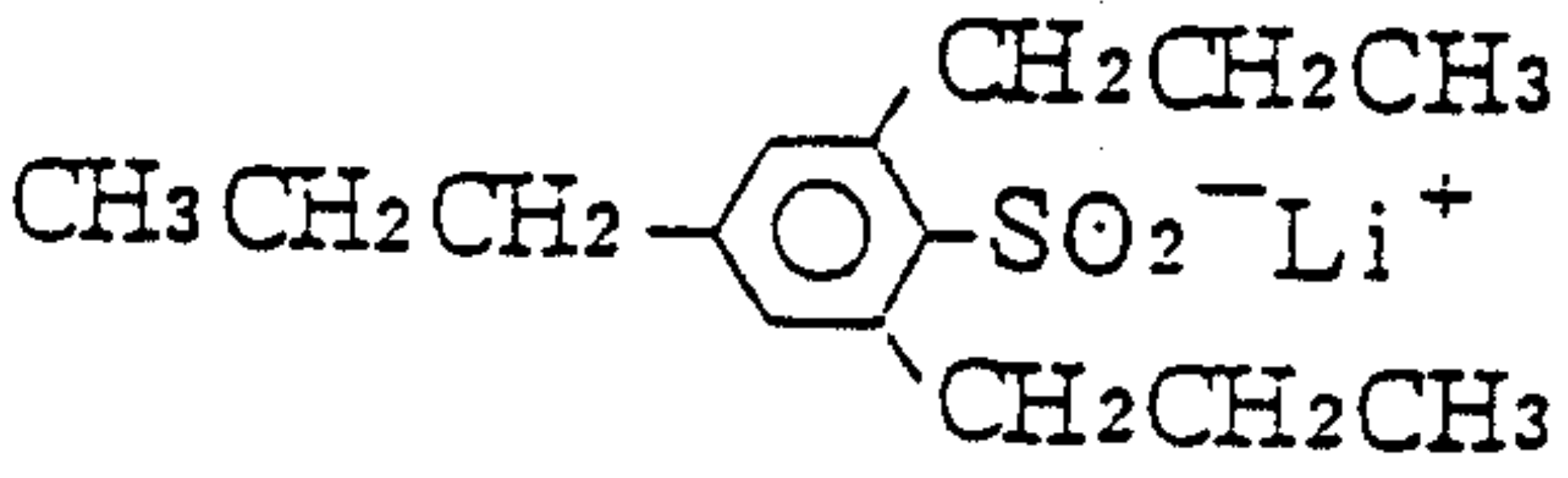
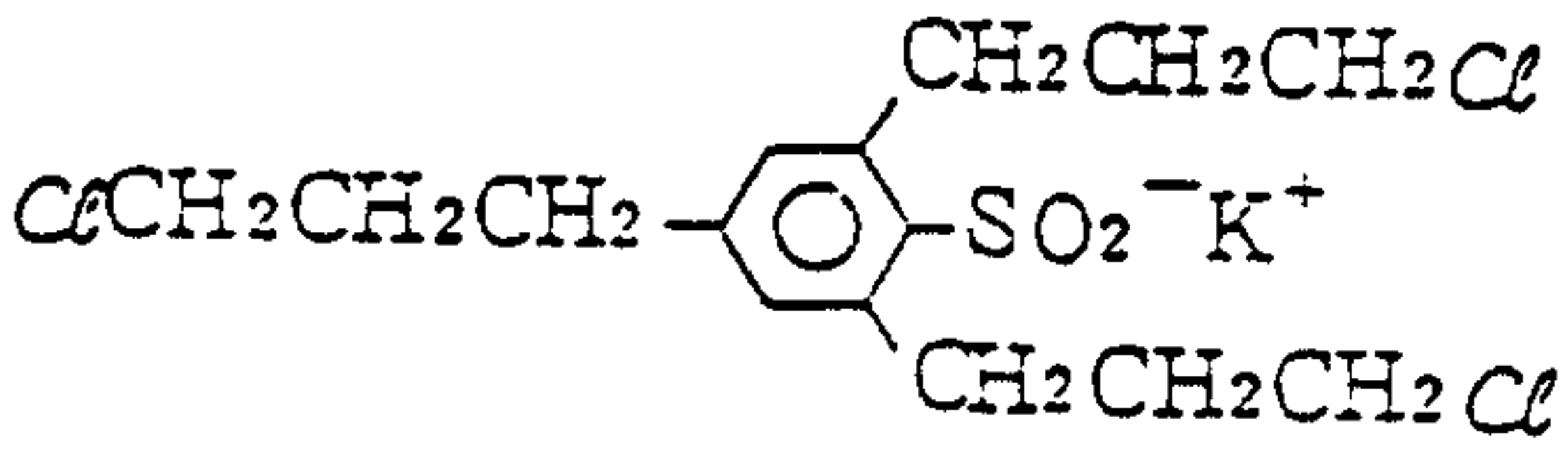
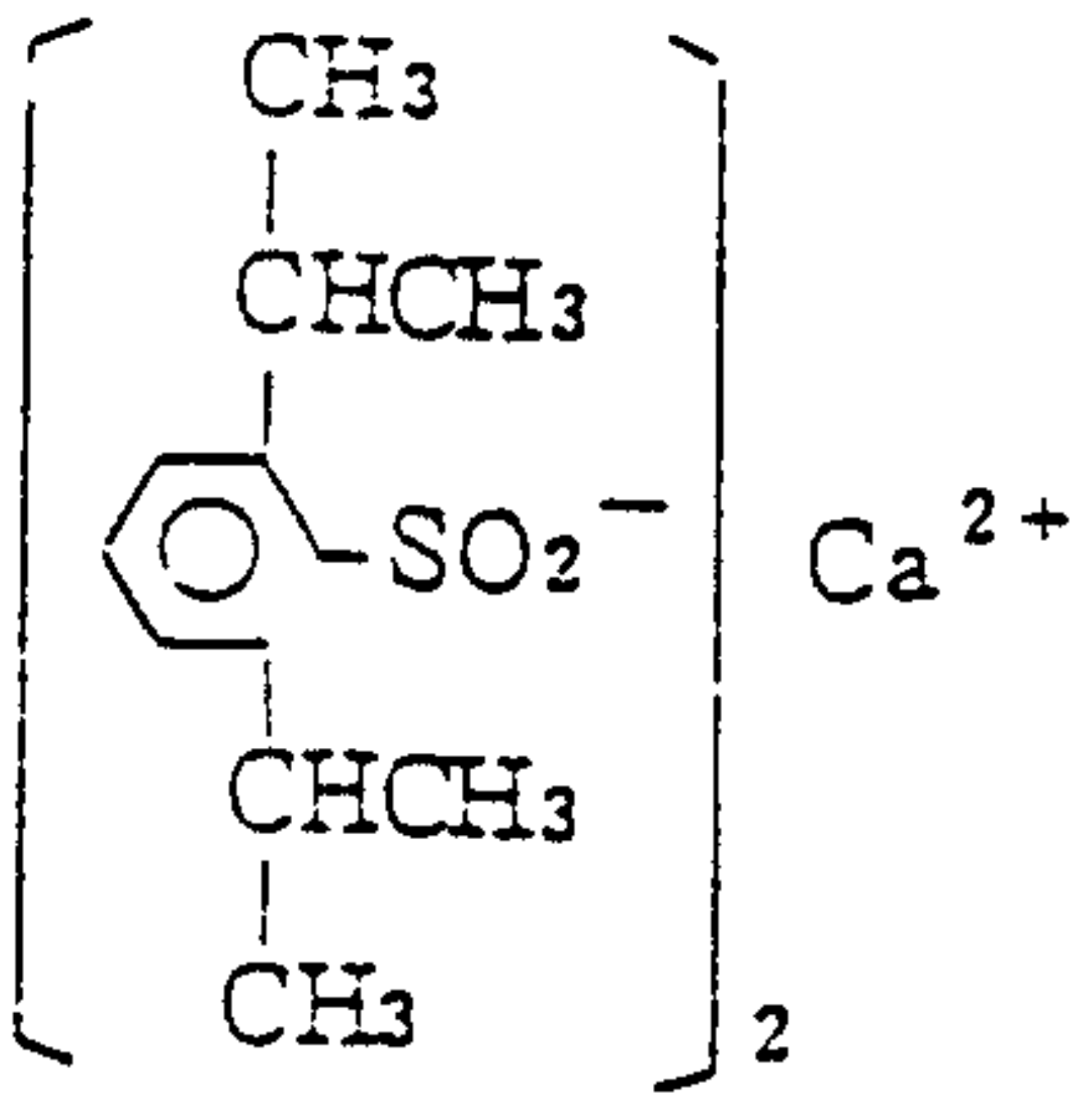
Preferred counter ions among these ions are Li^+, Na^+, K^+, Mg^{2+} and Ca^{2+}, since sulfinates therefrom are excellent in stability when stored in monomers and have good solubility in the monomers.

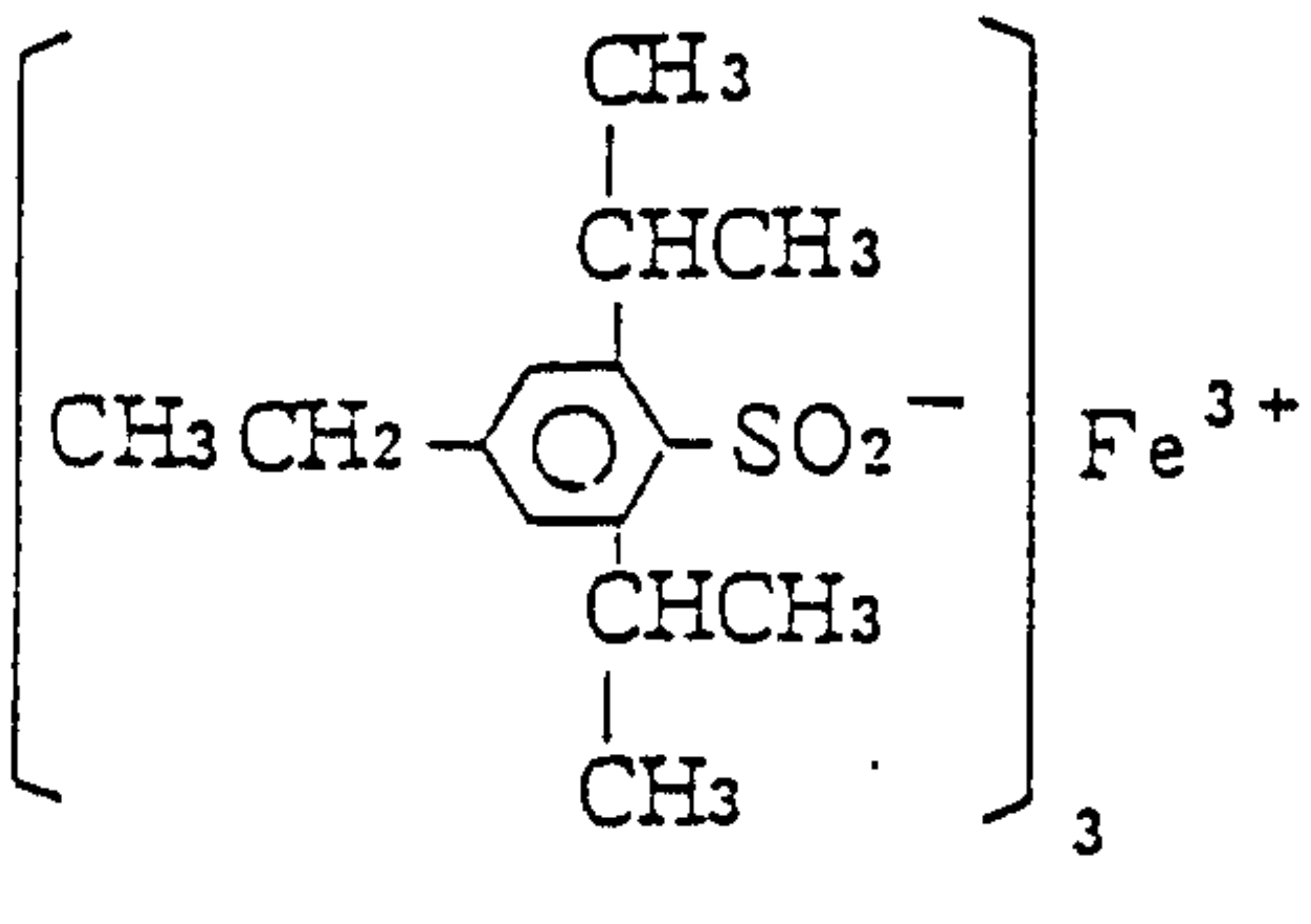
Examples of the sulfinate represented by general formula [I] are as follows.

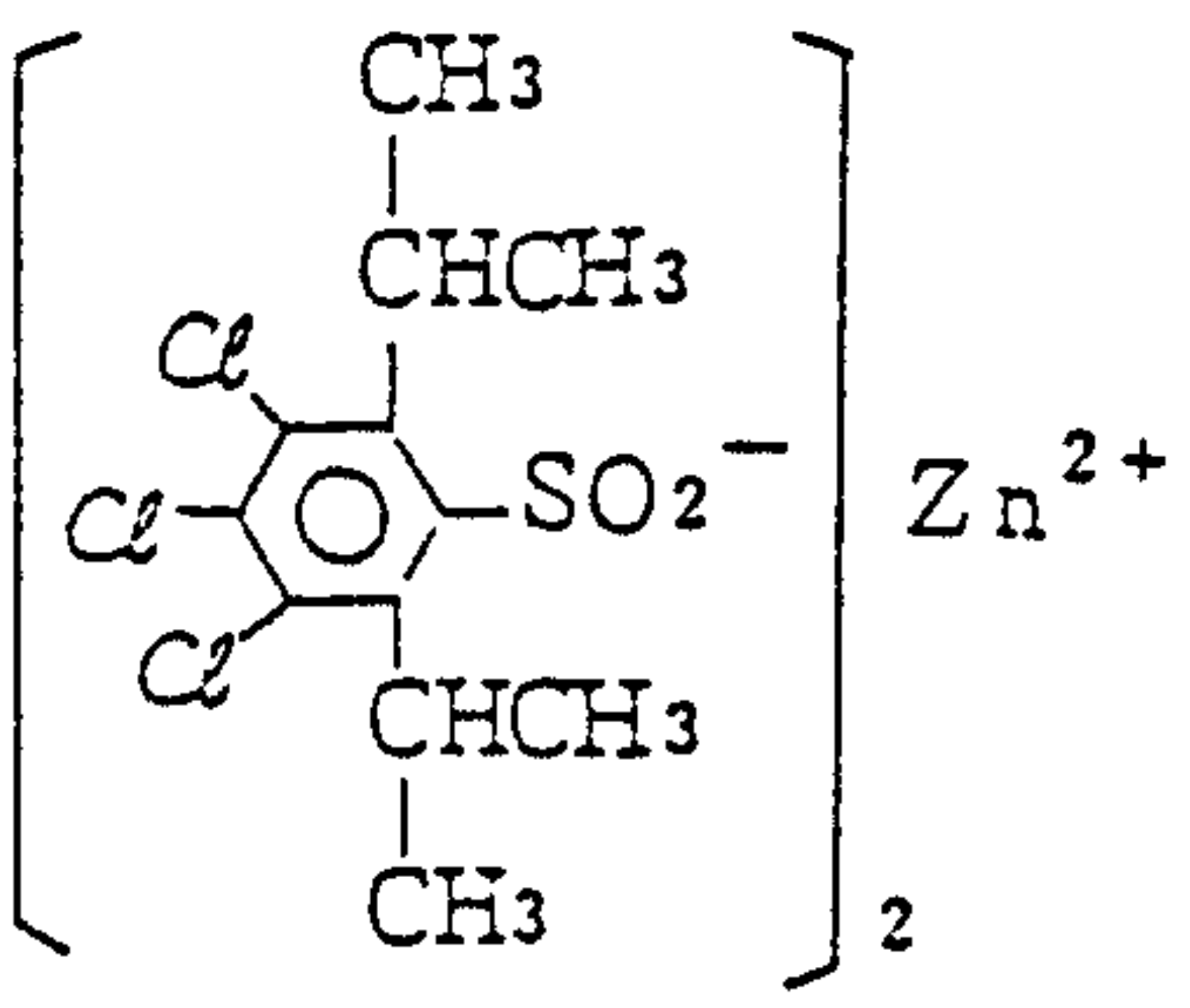


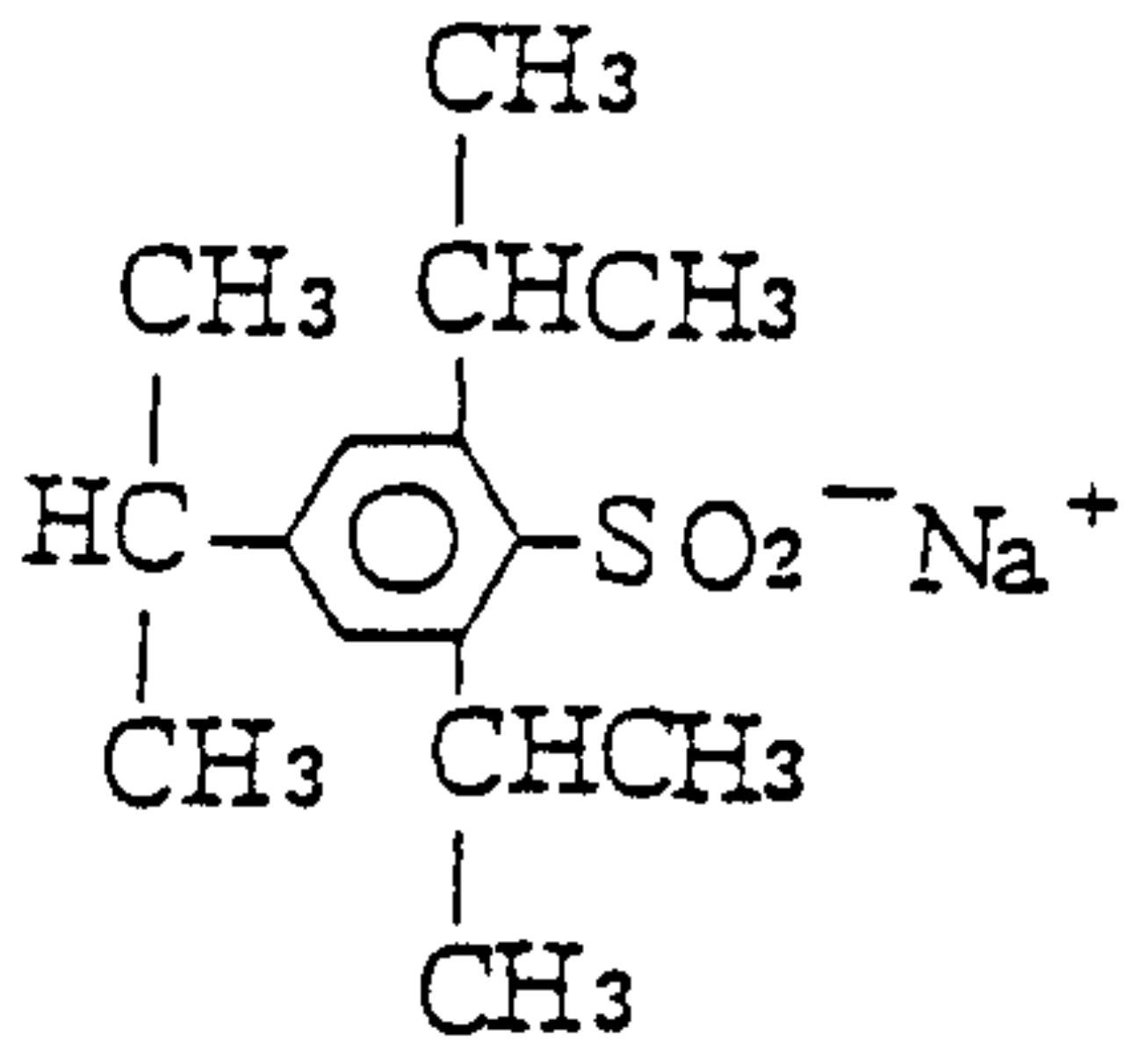


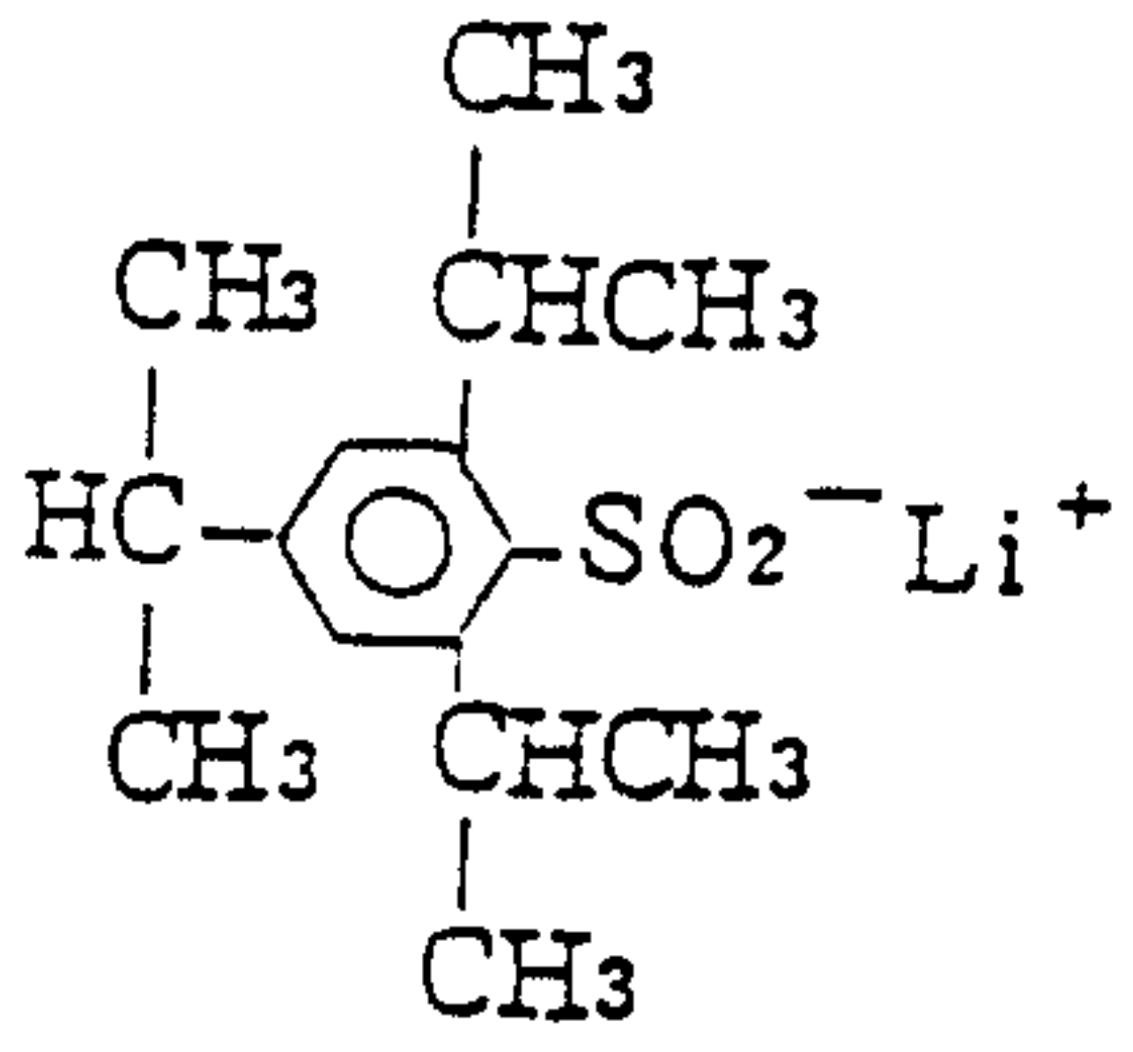


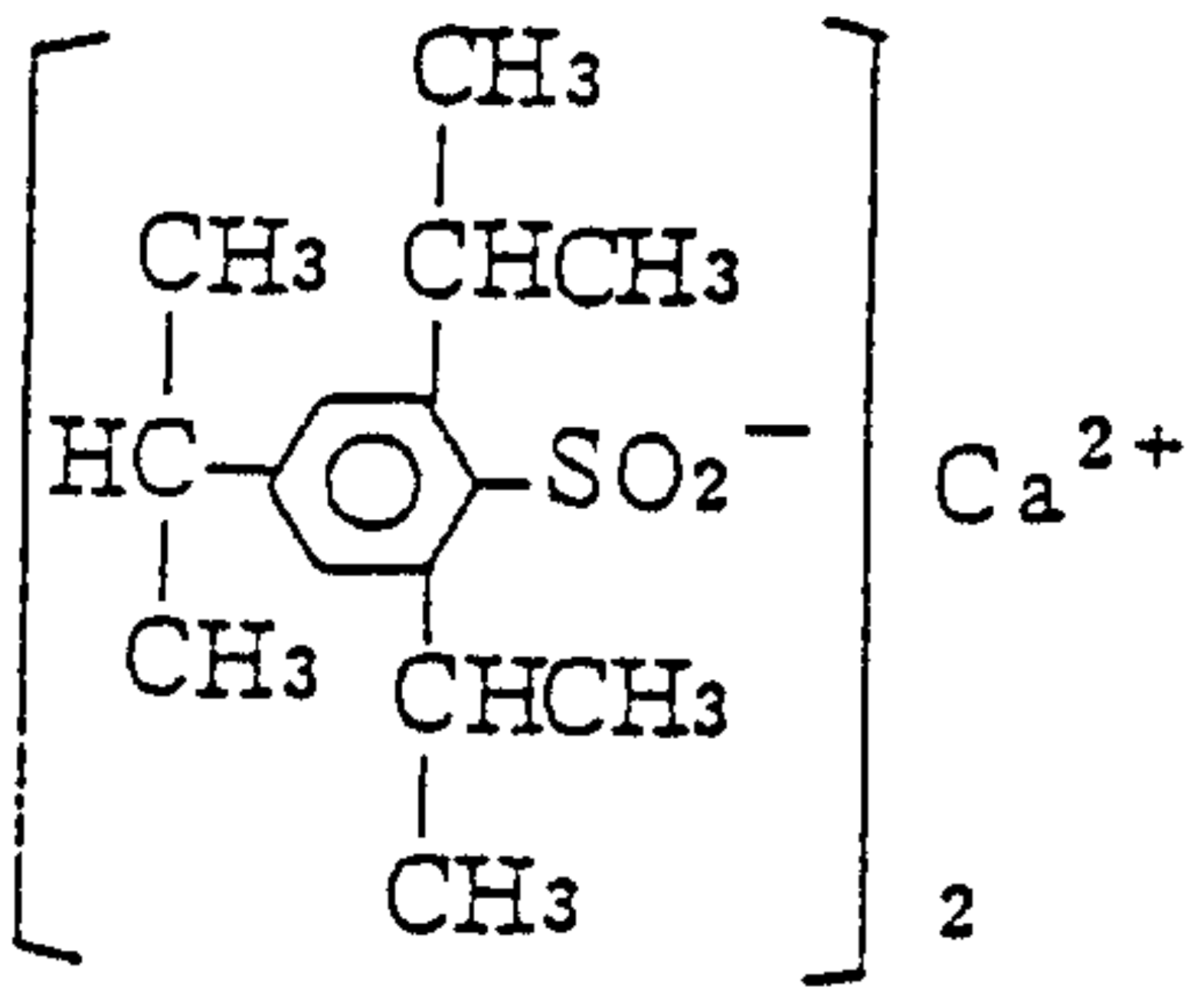


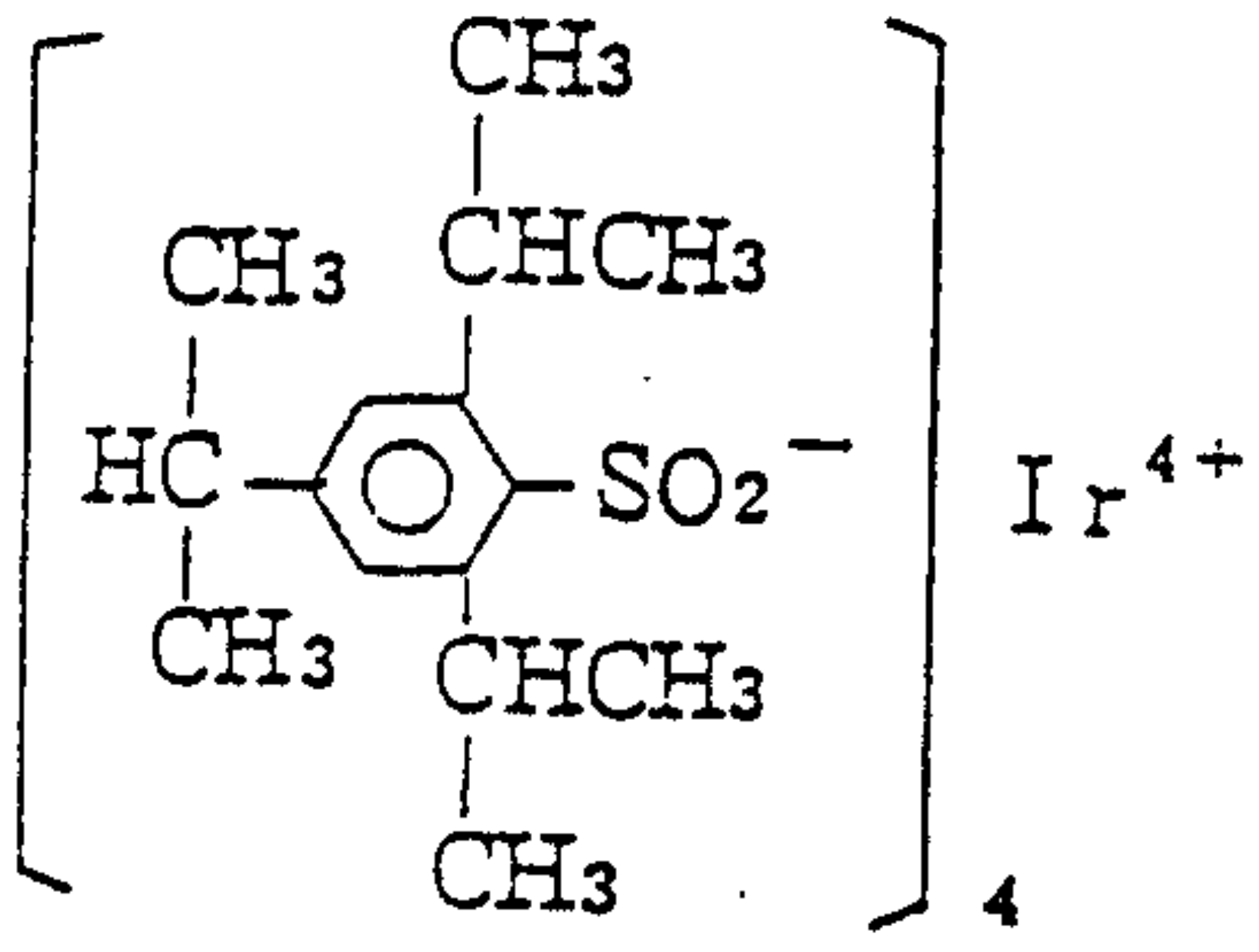


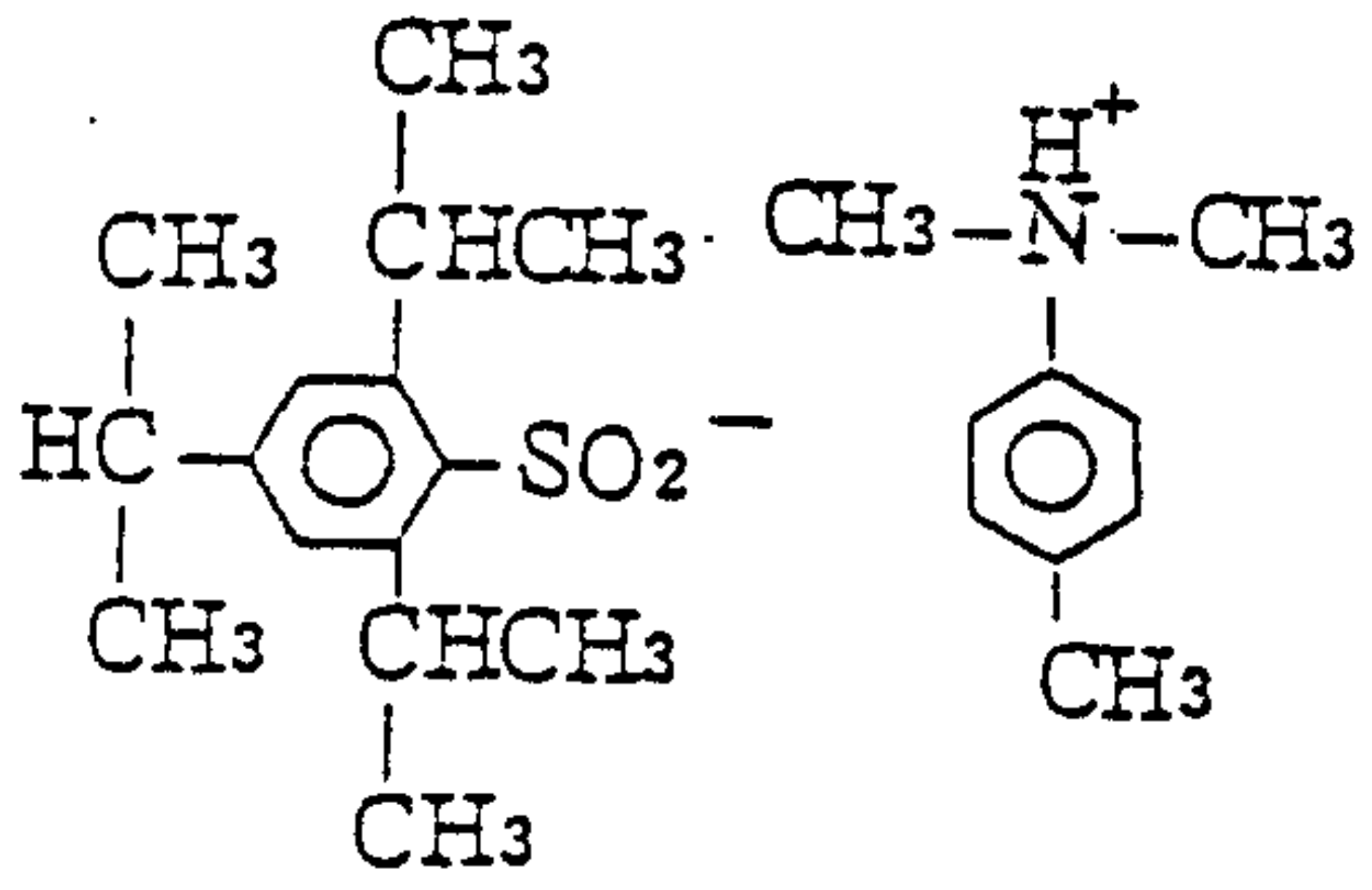


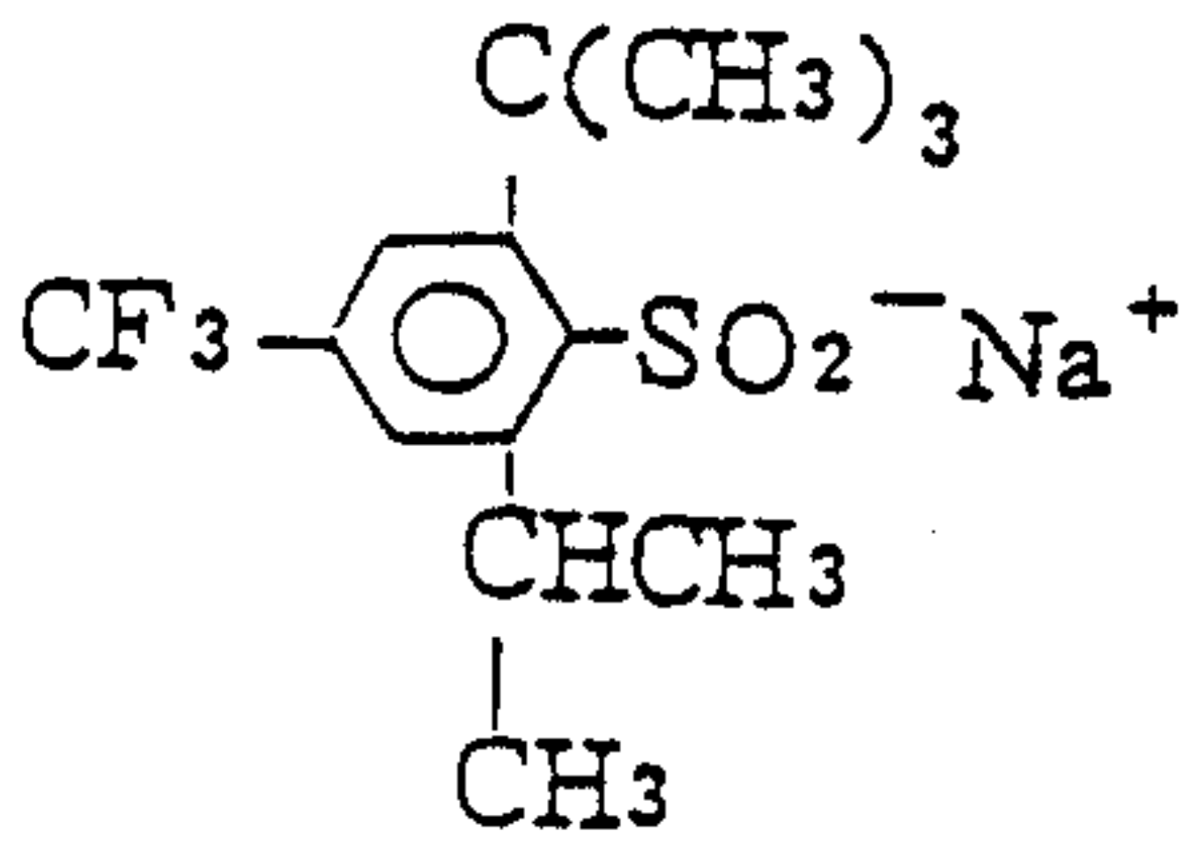

CH3
CH3 CHCH3
HC
SO2⁻Na⁺
CH3 CHCH3
CH3

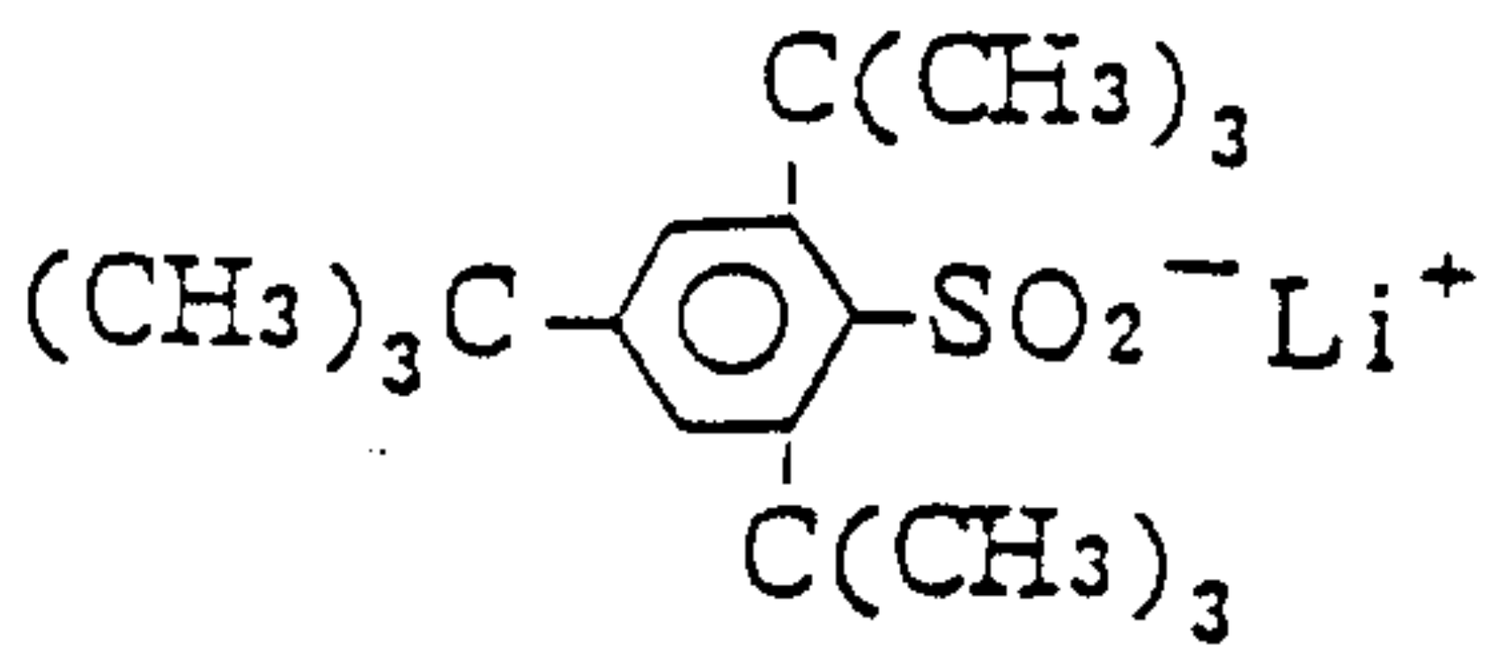

CH3
CH3 CHCH3
HC
SO2⁻Li⁺
CH3 CHCH3
CH3

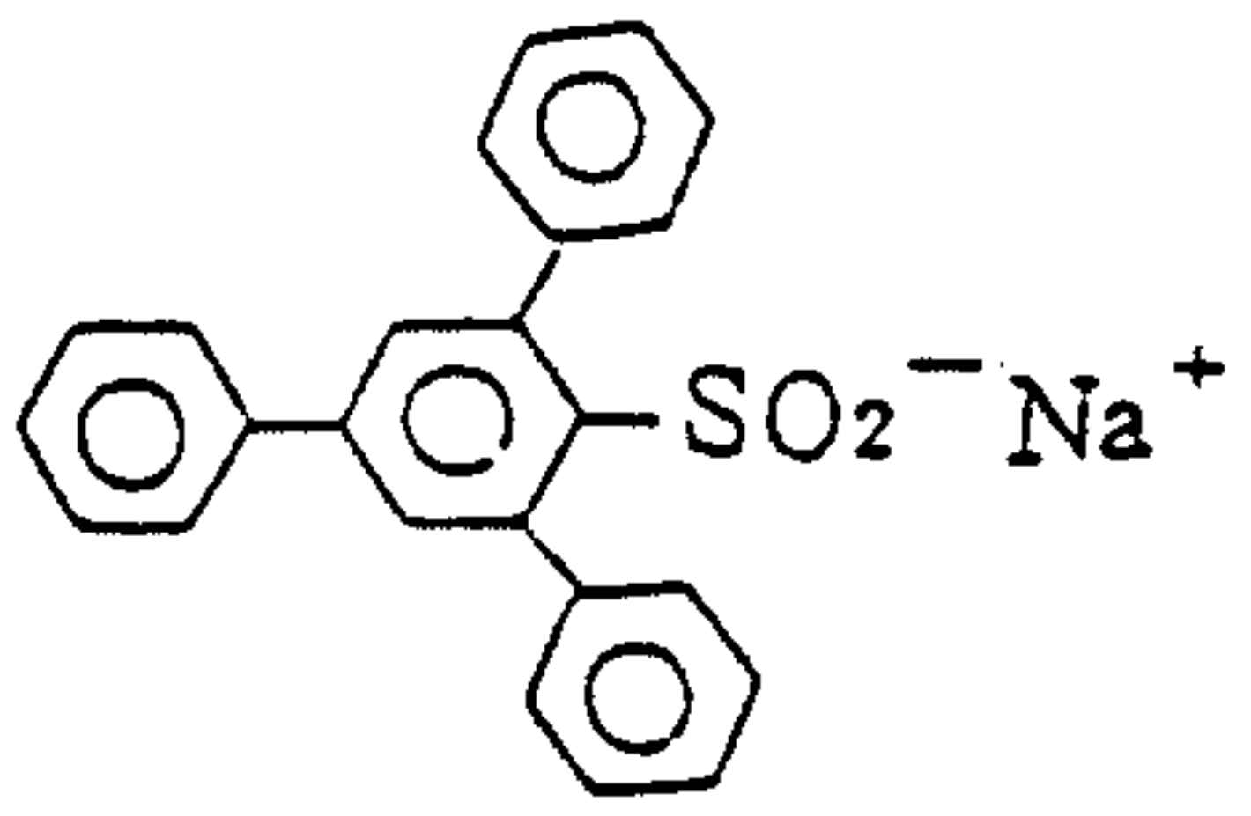

CH3
CH3 CHCH3
HC
SO2⁻
Ca²⁺
CH3 CHCH3
CH3
2

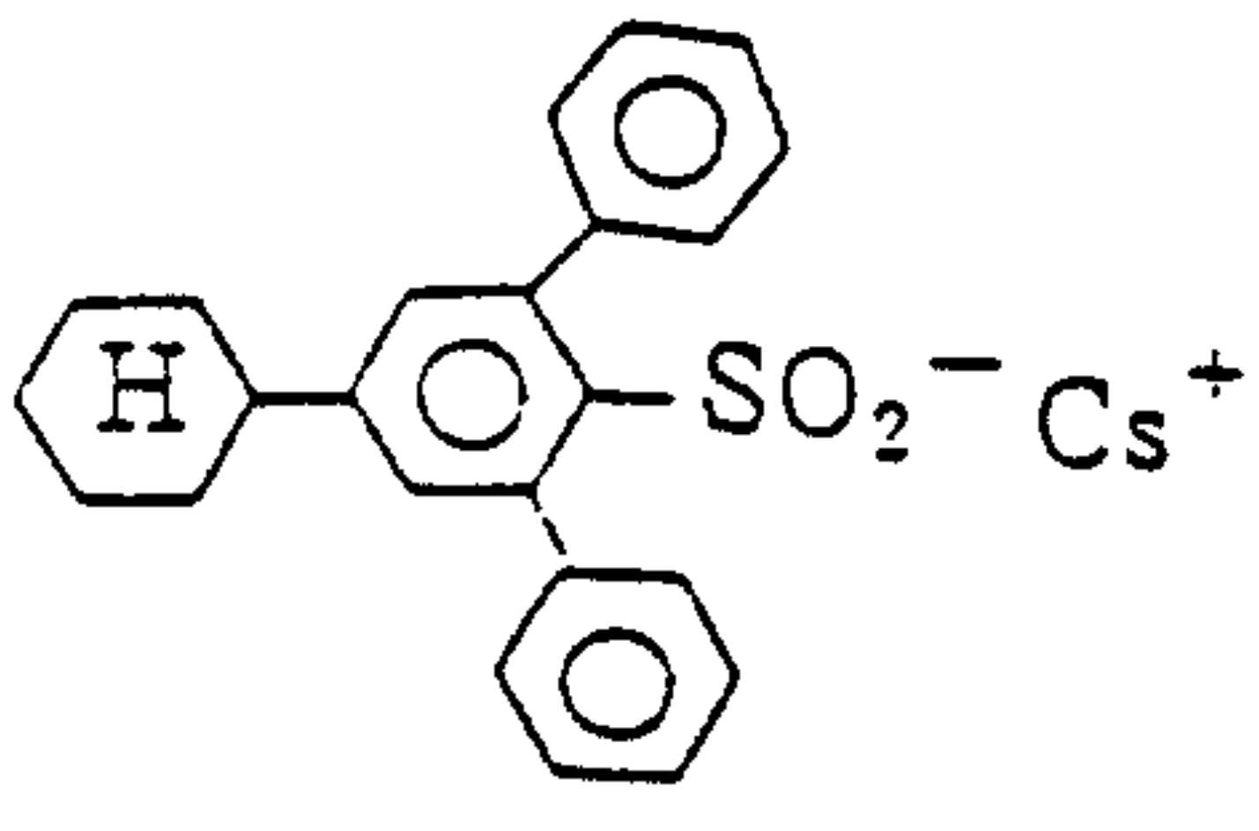

CH3
CH3 CHCH3
HC
SO2⁻
Ir⁴⁺
CH3 CHCH3
CH3
4


CH3
CH3 CHCH3
H⁺
CH3–N–CH3
HC
SO2⁻
CH3 CHCH3
CH3
CH3


C(CH3)3
CF3
SO2⁻Na⁺
CHCH3
CH3

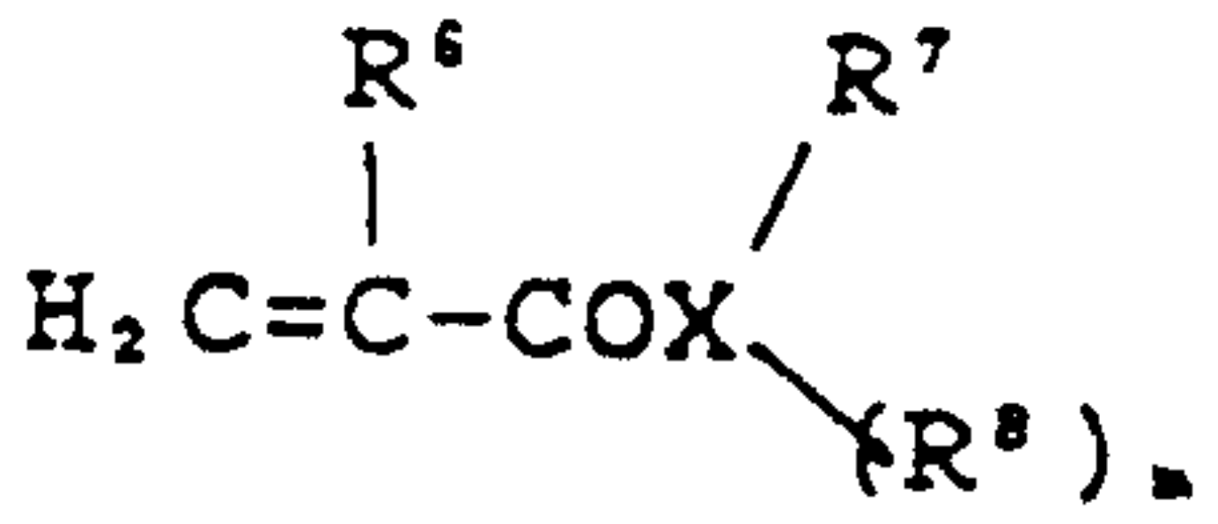

C(CH3)3
(CH3)3C
SO2⁻Li⁺
C(CH3)3


SO2⁻Na⁺


H
SO2⁻Cs⁺

The feature of the present invention appears most with the use of monomers having a carbon-to-carbon double bond directly linked to an electron attractive group such as -F, -Cl, -Br, -I, -CN, $-NO_2$, -NO, -CO-, -CS-, -COO-, -COS-, -CSO-, -CSS-, $-CONH_2$, -CONH- or -CON-. Where monomers without the above electron attractive groups, such as styrene, butadiene and allyl alcohol are used, sufficient storage stability is secured with conventional benzenesulfinates and toluenesulfinates. With monomers having the above electron attractive groups, these conventional sulfinates, however, cannot achieve practical storage stability because of occurrence of addition reaction.

Among monomers having carbon-to-carbon double bond directly linked to an electron attractive group, particularly suited for the purpose of the present invention are (meth)acrylates, α-haloacrylates, (meth)acrylamides and derivatives thereof, represented by the general formula



$$H_2C=\overset{\overset{R^6}{|}}{C}-COX\begin{matrix}\diagup R^7\\ \diagdown (R^8)_m\end{matrix}$$

wherein R^6 represents a hydrogen atom, methyl group or halogen atom, R^7 and R^8 each represents a hydrogen atom or an organic group which may contain $H_2C=\overset{\overset{R^6}{|}}{C}-COX-$, X represents an oxygen atom or nitrogen atom and m represents 0 where X is an oxygen atom and represents 1 where X is a nitrogen atom.

Examples of the monomer represented by the above general formula are as follows. In the present invention the expression "(meth)acryl" means both methacryl and acryl.

(a) Monofunctional (meth)acrylates

Methyl (meth)acrylate, ethyl (meth)acrylate, iso-butyl (meth)acrylate, n-hexyl (meth)acrylate, benzyl (meth)acrylate, decyl (meth)acrylate, lauryl (meth)acrylate, 2-hydroxyethyl (meth)acrylate, 2-(N,N-dimethylamino)ethyl (meth)-acrylate, 2,3-dibromopropyl (meth)acrylate, oxiranylmethyl (meth)acrylate, 3-methacryloyloxypropyltrimethoxysilane and the like.

(b) Bifunctional (meth)acrylates

Ethylene glycol di(meth)acrylate, diethylene glycol di(meth)acrylate, triethylene glycol di(meth)acrylate, propylene glycol di(meth)acrylate, dipropylene glycol di(meth)acrylate, neopentyl glycol di(meth)acrylate, 1,6-hexanediol di(meth)acrylate, 1,10-decanediol di(meth)acrylate, bisphenol-A-di(meth)acrylate, 2,2-bis((meth)acryloyloxyethoxyphenyl)propane, 2,2-bis((meth)acryloyloxypolyethoxyphenyl)propane, 2,2-bis[4-(3-(meth)acryloyloxy-2-hydroxypropoxy)phenyl]propane, 1,2-bis(3-(meth)acryloyloxy-2-hydroxypropoxy)ethane and the like.

(c) Tri- or more functional (meth)acrylates

Trimethylolpropane tri(meth)acrylate, trimethylolethane tri(meth)acrylate, tetramethylolmethane tri(meth)acrylate, pentaerythritol tetra(meth)acrylate and the like.

(d) α -Haloacrylates

α-Fluoromethyl acrylate, α-chloromethyl acrylate, α-fluoroethyl acrylate, α-chlorobutyl acrylate, α-fluoro-2,2,2-trifuloroethyl acrylate, and the like.

(e) (Meth)acrylamide derivatives

(Meth)acrylamide, N-methyl(meth)acrylamide, N-isopropyl-(meth)acrylamide, N-n-octyl(meth)acrylamide, N-benzyl(meth)-acrylamide, N-(2-hydroxyethyl)(meth)acrylamide, N-(2-dimethylaminoethyl)(meth)acrylamide, N,N-dimethyl(meth)acrylamide, N,N-dicyclohexyl(meth)acrylamide, N-methyl-N-phenyl(meth)acrylamide, N,N'-methylenebis(meth)acrylamide, 1,6-bis(meth)acrylamidehexane, and the like.

These copolymerizable monomers may be used singly or in combination.

The composition of the present invention is obtained by dissolving or suspending the compound represented by general formula [I] in the above monomer. The sulfinate represented by formula [I] is preferably used in an amount of 0.01 to 10% by weight based on the weight of the composition, more preferably in an amount of 0.03 to 5% by weight on the same basis.

Since the composition of the present invention is by itself extremely slow in initiating polymerization at room temperature, polymerization is effected by adding an oxidizer or by adding a photoinitiator, followed by photoradiation.

As the oxidizer used in the invention, organic peroxides capable of initiating polymerization by redox reaction with sulfinates are employed, and diacyl peroxides are preferred. Examples of the diacyl peroxides include, among others, benzoyl peroxide, m-toluoyl peroxide, 2,4-dichloro-benzoyl peroxide, octanoyl peroxide, lauroyl peroxide and succinoyl peroxide, among which particularly preferred are aromatic peroxides such as benzoyl peroxide and m-toluoyl peroxide. The oxidizer is stored in a package avoiding contact with the sulfinate represented by formula [I], and is, in polymerizing the composition of the present invention, added to the sulfinate in an amount of 0.01 to 500 parts by weight based on 1 parts by weight of the sulfinate. An amine may further be added to the sulfinate and oxidizer system to form a ternary initiator, whereby polymerization is much more accelerated. In this case, while the amine can be stored while being in contact with the sulfinate with no problem, the amine must not contact the oxidizer for inhibition of premature polymerization. In packaging the sulfinate and the oxidizer separately, the amine is therefore packed together with the sulfinate. Aromatic secondary or tertiary amines are preferred for this purpose, and their examples are N,N-dimethylaniline, N,N-dimethyl-p-toluidine, ethyl m-N,N-dimethylaminobenzoate, ethyl p-N,N-dimethylaminobenzoate, N,N-diethanolaniline, N,N-diethanol-p-toluidine, N,N-diethanol-m-chloroaniline, N,N-bis(3-hydroxypropyl)aniline, N,N-bis(3-hydroxypropyl)-p-toluidine, N,N-bis(2,3-dihydroxypropyl)aniline, N,N-bis(2,3-dihydroxypropyl)-p-toluidine, ethyl m-N,N-bis(2,3-dihydroxypropyl)aminobenzoate, N-methylaniline, N-methyl-p-toluidine.

The amine is added in an amount of 0.01 to 500 parts by weight based on 1 part by weight of the compound represented by formula [I].

Suitable photoinitiators are photosensitive dyes and α-diketones, and their examples are Methylene blue, Eosin YS, diacetyl, 2,3-pentanedione, 2,3-hexanedione, 3,4-hexanedione, camphorquinone, bicyclo-[2.2.1]heptane-2,3-dione, acenaphthenequinone, 9,10-phenanthraquinone, 9,10-anthraquinone and the like. The photoinitiator is added in an amount of 0.01 to 500 parts by weight based on 1 part by weight of the compound of formula [I].

The composition of the present invention can comprise both the oxidizer and the photoinitiator and be subjected to both redox and photopolymerization.

On the other hand, where the composition of the present invention is used as a primer, on which another polymerizable composition is applied, polymerization is effected by an initiator which has been contained in the other polymerizable composition and has migrated to the composition of the present invention, even when the composition of the present invention has not originally contained an oxizer or photoinitiator.

The composition of the present invention may further comprise, as required, additives other than the above components, such as inorganic filler, polymer, organic solvent, polymerization inhibitor, antioxidant, ultraviolet absorber, pigment, dye and the like. When a polymer is added, it can be added either as an insoluble filler or as a thickener, which is soluble in the composition.

As stated heretofore, introduction of bulky groups into positions 2 and 6 of a benzenesulfinate can suppress the rate of addition reaction of the sulfinate to the double bond of the monomer down below 1/10 that in the case conventional benzenesulfinates or toluenesulfinates are used. Then, while compositions comprising conventional sulfinates can be stored at room temperature stably only for a few weeks, the compositions of the present invention can be stored at room temperature stably for at least one year and thus have significant practical advantage.

The polymerizable composition of the present invention can polymerize rapidly by addition of an oxidizer or by addition of a photoinitiator, followed by photoradiation. The present composition can be used as adhesives for various industrial uses and as moldable resins. One of the suitable uses of the composition is for dental field, where it is used as dental adhesive.

Other features of the invention will become apparent in the course of the following descriptions of exemplary embodiments which are given for illustration of the invention and are not intended to be limiting thereof.

EXAMPLES

Examples 1 through 7 and Comparative Examples 1 through 8

There were used as the sulfinates, sodium 2,4,6-triethylbenzenesulfinate, sodium 2,4,6-triisopropylbenzenesulfinate, lithium 2,4,6-triisopropylbenzenesufinate, calcium 2,6-diisopropylbenzenesulfinate, lithium 2,4,6-tri-tert-butylbenzenesulfinate and sodium 2,4,6-triphenylbenzenesulfinate, and, as the polymerizable monomers, 2-hydroxyethyl methacrylate and a mixture of 2,2-bis[4-(3-methacryloyloxy-2-hydroxypropoxy)phenyl]propane, triethylene glycol dimethacrylate and 1,2-bis(3-methacryloyloxy-2-hydroxypropoxy)ethane, to prepare compositions of Examples 1 through 7 as shown in Table 1. These compositions were each placed in a glass ampule tube, which was then sealed by fusion, and the tubes with their contents were stored at 37°C for 14 days. The amounts of the sulfinates before and after the storage were determined by high-performance liquid chromatography, and the ratios of remaining sulfinates after the storage at 37°C for 14 days were calculated. The results are shown in Table 1. The above procedures were repeated except for using, instead of the sulfinates used in Examples 1 through 7, sodium benzenesulfinate, sodium p-toluenesulfinate, sodium p-ethylbenzenesulfinate, sodium p-isopropylbenzenesulfinate, calcium p-isopropylbenzenesulfinate, calcium o-isopropylbenzenesulfinate and sodium 2,4,6-trimethylbenzenesulfinate, to prepare compositions of Comparative Examples 1 through 8.

Regardless of absence or presence, or the type, of substituent in position 4, introduction of substituents having at least 2 carbon atoms into positions 2 and 6 significantly increased the retention of sulfinate. Where a substituent having at least 2 carbon atoms was introduced into only position 2 and where methyl groups were introduced into positions 2 and 6, there were observed some improvement in retention, which fell, however, far short of the retention achieved in the case where substituents having at least 2 carbon atoms were introduced in both positions 2 and 6.

Table 1

	Components of Composition				Retention of sulfinate (%)
	Monomer;	parts by weight	Sulfinate;	parts by weight	
Example 1	2-hydroxyethyl methacrylate	100	sodium 2,4,6-triethylbenzenesulfinate	1	82
〃 2	2-hydroxyethyl methacrylate	100	sodium 2,4,6-triisopropylbenzenesulfinate	1	90
〃 3	2-hydroxyethyl methacrylate	100	lithium 2,4,6-triisopropylbenzenesulfinate	1	92
〃 4	2-hydroxyethyl methacrylate	100	lithium 2,4,6-tri-tert-butylbenzenesulfinate	1	95
〃 5	2-hydroxyethyl methacrylate	100	sodium 2,4,6-triphenylbenzenesulfinate	1	97
〃 6	2,2-bis[4-(3-methacryloyloxy-2-hydroxypropoxy)phenyl]propane triethylene glycol dimethacrylate 1,2-bis(3-methacryloyloxy-2-hydroxypropoxy)ethane	40 30 30	sodium 2,4,6-triisopropylbenzenesulfinate	1	96
〃 7	2,2-bis[4-(3-methacryloyloxy-2-hydroxypropoxy)phenyl]propane triethylene glycol dimethacrylate 1,2-bis(3-methacryloyloxy-2-hydroxypropoxy)ethane	40 30 30	calcium 2,6-diisopropylbenzenesulfinate	1	98

Table 1 (continued)

	Components of Composition				Retention of sulfinate (%)
	Monomer;	parts by weight	Sulfinate;	parts by weight	
Comparative Example 1	2-hydoxyethyl methacrylate	100	sodium benzenesulfinate	1	10
〃 2	2-hydoxyethyl methacrylate	100	sodium p-toluenesulfinate	1	8
〃 3	2-hydoxyethyl methacrylate	100	sodium p-ethylbenzenesulfinate	1	8
〃 4	2-hydoxyethyl methacrylate	100	sodium p-isopropylbenzenesulfinate	1	7
〃 5	2-hydoxyethyl methacrylate	100	calcium p-isopropylbenzenesulfinate	1	9
〃 6	2-hydoxyethyl methacrylate	100	calcium o-isopropylbenzenesulfinate	1	38
〃 7	2-hydoxyethyl methacrylate	100	sodium 2,4,6-trimethylbenzenesulfinate	1	55
〃 8	2,2-bis[4-(3-methacryloyloxy-2-hydroxypropoxy)phenyl]propane triethylene glycol dimethacrylate 1,2-bis(3-methacryloyloxy-2-hydroxypropoxy)ethane	40 30 30	sodium benzenesulfinate	1	13

Example 8 and Comparative Example 9

The following compositions A and B were prepared.

Composition A	Parts by weight
2,2-Bis[4-(3-methacryloyloxy-2-hydroxypropoxy)phenyl]propane	40
Triethylene glycol dimethacrylate	30
2-Hydroxyethyl methacrylate	30
Sodium 2,4,6-triisopropylbenzenesulfinate	1
N,N-Diethanol-p-toluidine	2
Quartz powder silane-treated	300
Composition B	
2,2-Bis[4-(3-methacryloyloxy-2-hydroxypropoxy)phenyl]propane	40
Triethylene glycol dimethacrylate	30
10-Methacryloyloxydecyl dihydrogenphosphate	30
Benzoyl peroxide	2
Quartz powder silane-treated	300

The composition A just after preparation and that after having been stored at 25°C for 1 year were each subjected to the following test 1. Further these were combined with composi-tion B and subjected to the following tests 2, 3 and 4.

Test 1

To 0.5 g of composition A 5 ml of methanol was added, the mixture was stirred well and the quartz powder was removed from the mixture by filtration. The amount of sodium 2,4,6-triisopropylbenzenesulfinate in the methanol solution was determined by high-performance liquid chromatography. The ratio of amount of sodium 2,4,6-triisopropylbenzene-sulfinate after storage to that just after preparation was calculated. The results are shown in Table 2.

Test 2

Equal amounts of compositions A and B were kneaded together for 30 seconds, and the mixture was filled in a teflon container having an inside diameter of 5 mm and a depth of 7 mm, and tested for curing or hardening time. A thermocouple was inserted in the kneaded mixture and temperature change was recorded. Time required until the stoppage of temperature increase due to polymerization heat was taken as the curing time. The results are shown in Table 2.

Test 3

A test surface to be bonded was prepared by patching an adhesive tape with a hole having a diameter of 5 mm to the surface of a nickel-chrome alloy plate (Now Chrom$^{\text{TM}}$ (I), made by Towa Giken Co.) ground with 1000-grit silicon-carbide abrasive paper. Round rods of SUS304 and having a diameter of 7 mm and a length of 25 mm were sand blasted on their end surface with a lumina abrasive powder of particle size of 50 μm. On the blasted end a paste obtained by kneading equal amounts of compositions A and B was heaped and the paste was pressed onto the test surface to bond the rod to the surface. After 1 hour the test piece thus prepared was immersed in water at 37°C and kept therein for 24 hours, and then tested for tensile bond strength using a universal tensile testing machine (Instron™) at a crosshead speed of 2 mm/min. An average of measurements on 10 test pieces was calculated. The results are shown in Table 2.

Test 4

A labial enamel surface of bovine tooth was ground with silicon-carbide abrasive paper to be flat, and the flat surface was etched with a 40% aqueous phosphoric acid solution for 1 minute. On the etched surface an adhesive tape with a hole having a diameter of 5 mm was patched to prepare a test surface to be bonded. Round rods of SUS304 and having a diameter of 7 mm and a length of 25 mm were sand blasted on their end surface with alumina abrasive powder of particle size of 50 μm. On the blasted end a paste obtained by kneading equal amounts of compositions A and B was heaped and the paste was pressed onto the test surface to bond the rod to the surface. After 1 hour the test piece thus prepared was immersed in water at 37°C and kept therein for 24 hours, and then tested for tensile bond strength using Instron at a crosshead speed of 2 mm/min. An average of measurements on 10 test pieces was calculated. The results are shown in Table 2.

This Example 8 was repeated except for preparing composition by using sodium benzenesulfinate instead of sodium 2,4,6-triisopropylbenzenesulfinate of composition A. This is Comparative Example 9 in Table 2.

Table 2

	Example 8		Comparative Example 9	
	Just after preparation	After storage at 25℃ for 1 year	Just after preparation	After storage at 25℃ for 1 year
Test 1 (Retention of suflinic acid salt) (%)	100	89	100	0
Test 2 (Curing time)	8 min and 30 sec	8 min and 55 sec	8 min and 35 sec	not hardened
Tast 3 (Bond strength to nickel-chrome alloy) (kg/cm^2)	419	408	420	not tested because this did not harden.
Test 4 (Bond strength to bovine tooth enamel) (kg/cm^2)	160	156	159	not tested because this did not harden.

Example 9

The following composition C was prepared.

Composition C	Parts by weight
2,2-Bis[4-(3-methacryloyloxy-2-hydroxypropoxy)phenyl]propane	40
1,6-Bismethacrylamidehexane	30
2-Hydroxyethyl methacrylate	30
Sodium 2,4,6-triisopropylbenzenesulfinate	1
Camphorquinone	1

A glass cylindrical sample tube having an inside diameter of 10 mm and a wall thickness of 0.8 mm was charged with 0.25 ml of the composition. The tube with its contents was irradiated from below through a visible light irradiator (Quick light™, made by Kuraray Co., Ltd.), then the contents hardened in 32 seconds. A part of the above composition was stored at room temperature for 1 year, and then subjected to the same irradiation test, to harden in 35 seconds. In determining the curing time, a thermocouple was inserted in the composition and temperature change was recorded. Time required until the stoppage of temperature increase due to polymerization heat was taken as the curing time.

Example 10

The following compositions D and E were prepared, and, after being stored at room temperature for 1 year, tested for adhesiveness to human tooth dentine.

Composition D	Parts by weight
2,2-Bis[4-(3-methacryloyloxy-2-hydroxypropoxy)phenyl]propane	20
2-Hydroxyethyl methacrylate	80
Sodium 2,4,6-triisopropylbenzenesulfinate	3
N,N-Dimethyl-p-toluidine	2
2,6-Di-t-butyl-4-methylphenol	0.03

Composition E	
2,2-Bis[4(3-methacryloyloxy-2-hydroxypropoxy)phenyl]propane	35
Neopentyl glycol dimethacrylate	30
10-Methacryloyloxydecyl dihydrogenphosphate	35
Benzoyl peroxide	2
2,6-Di-t-butyl-4-methylphenol	0.03

Human molar tooth was ground with a silicon-carbide abrasive paper to expose the dentine, and then acid-etched with a 40% aqueous phosphoric acid solution for 1 minute. An adhesive tape with a hole having a diameter of 5 mm was patched on this etched surface to prepare a test surface to be bonded. Separately, pieces of round rod of SUS304 and having a diameter of 7 mm and a length of 25 mm were sand blasted on their end surface with alumina abrasive powder of particle size of 50 μm. A paste obtained by kneading equal amounts of compositions D and E was applied both on this blasted end surface and on the human tooth test surface prepared above. Kneaded paste of a commercially available dental composite resin (CLEARFIL™ FII, made by Kuraray Co.)

was heaped on the end surface of the rod and the paste was pressed onto the human tooth test surface to bond the rod to the surface. After 1 hour the test piece thus prepared was immersed in water at 37°C and kept therein for 24 hours, and then tested for tensile bond strength using Instron at a crosshead speed of 2 mm/min. An average of measurements on 8 test pieces was calculated to give 130 kg/cm^2.

Example 11

The compositions D and E stored at room temperature for 1 year as used in Example 10 were tested for metal-to-metal adhesiveness as follows.

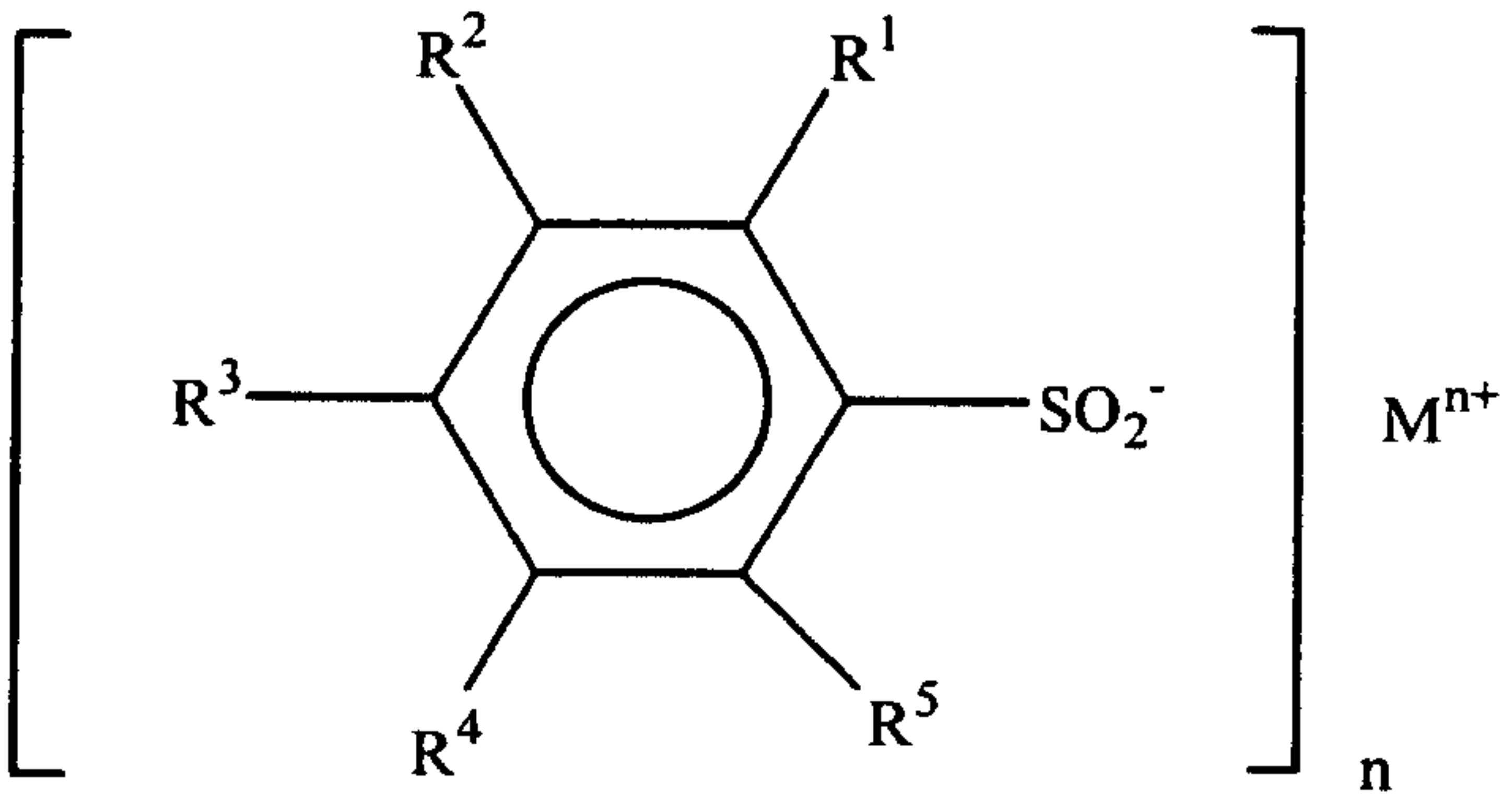
Two pieces of round rod of SUS304 and having a diameter of 7 mm and a length of 25 mm were sand blasted on their end surface with alumina grinding powder of particle size of 50μm. Composition D was applied to the blasted end surface of one rod, while composition E to that of the other rod. The two surfaces were pressed with each other to bond, to prepare a test piece. The test piece was kept at 25°C for 24 hours, and then tested for tensile bond strength with Instron at a crosshead speed of 2 mm/min. An average of measurements on 10 test pieces was 382 kg/cm^2.

Obviously, numerous modifications and variations of the present invention are possible in light of the above teachings. It is therefore to be understood that within the scope of the appended claims, the invention may be practiced otherwise than as specifically described herein.

What is claimed is:

1. A polymerizable composition comprising:

(a) a sulfinate initiator component represented by the general formula [I]

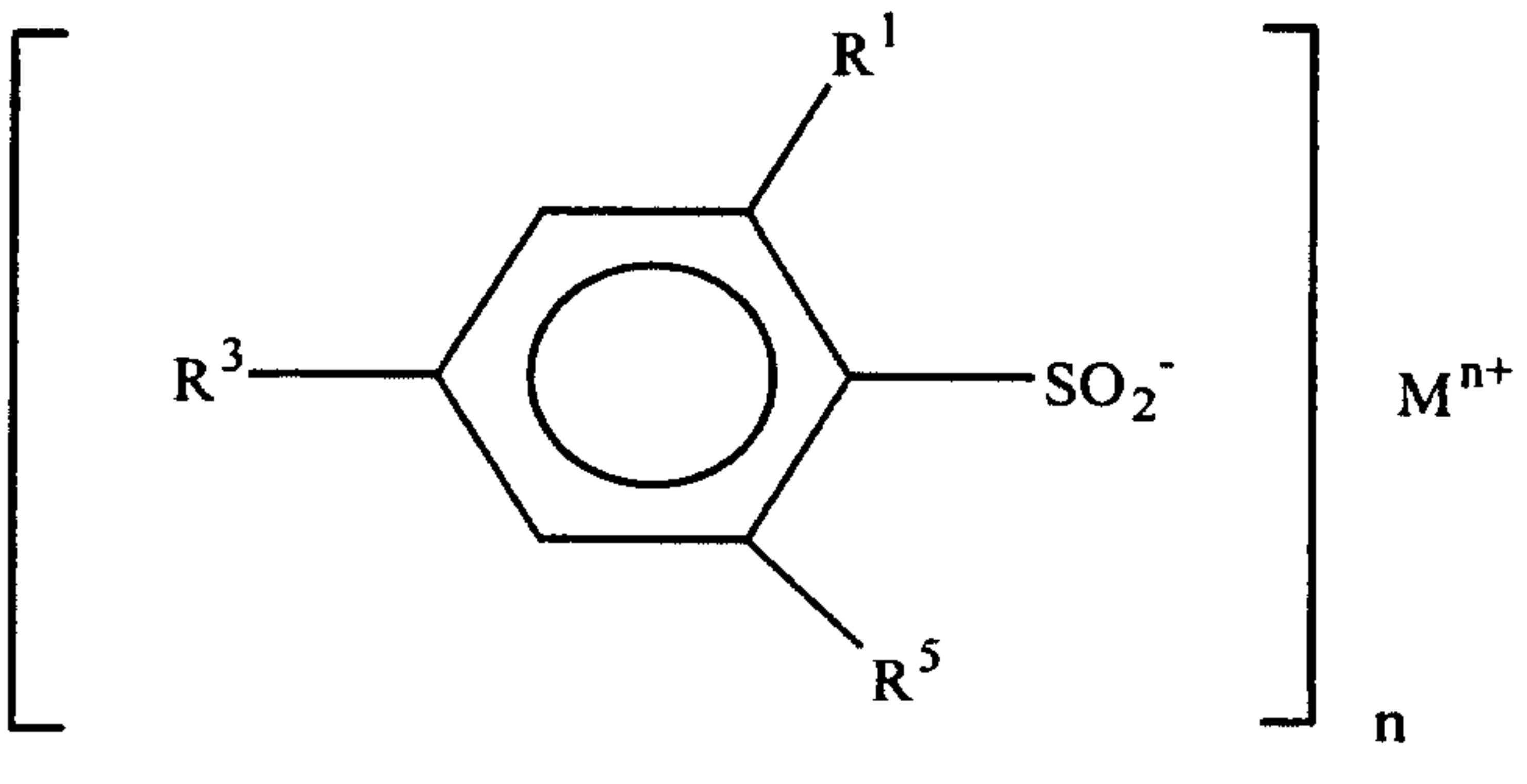


[I]

wherein R^1 and R^5 each represents a substituent having 2 to 6 carbon atoms, R^2, R^3 and R^4 each represents an atom or substituent inert to the below-described monomer (b), M^{n+} represents a n-valent cation, and n represents an integer of 1 to 4; and

(b) a monomer having at least one polymerizable carbon-carbon double bond.

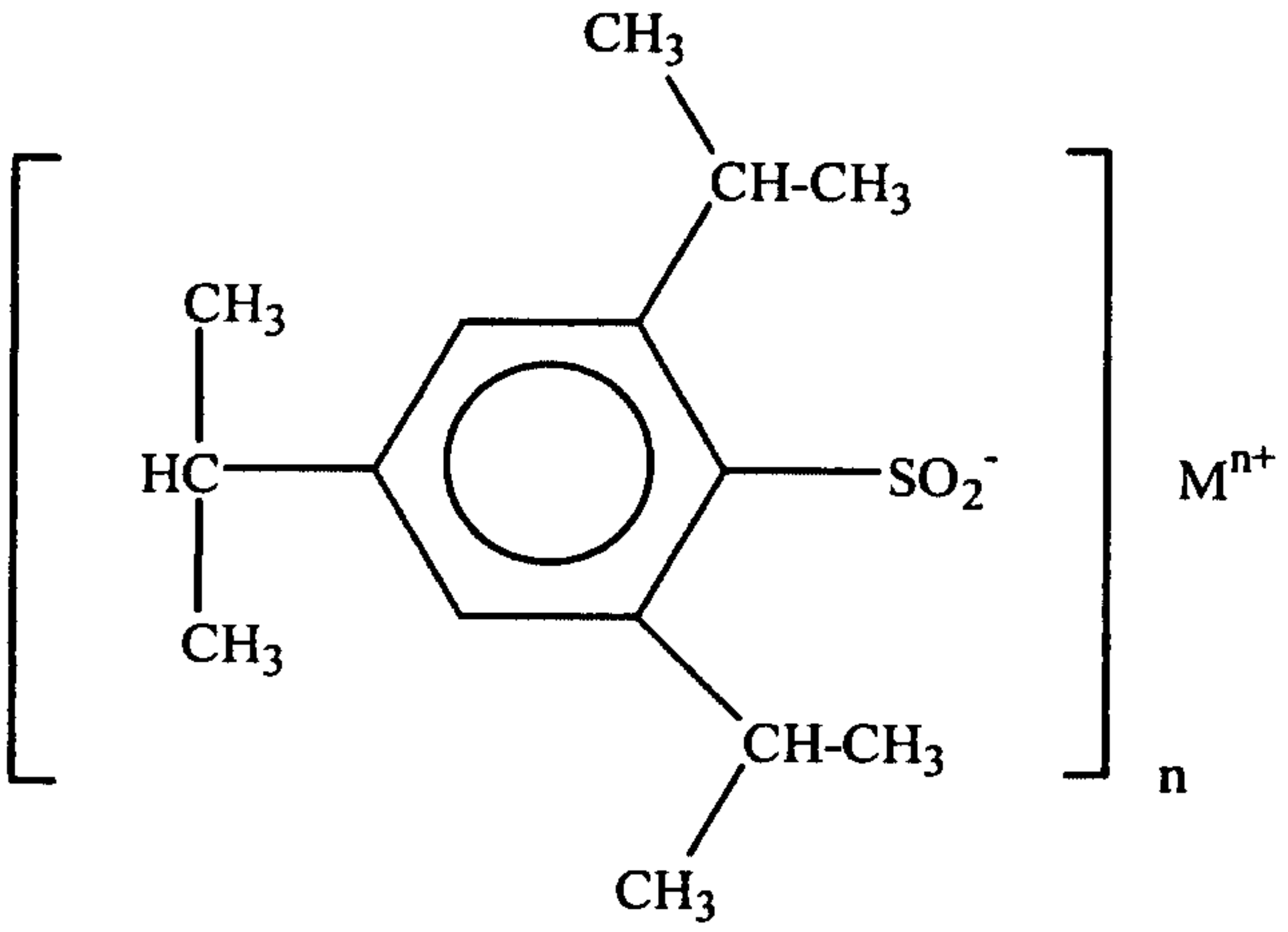
2. A polymerizable composition according to Claim 1, wherein said sulfinate initiator component is represented by the general formula



B

wherein R^1 and R^5 each represents a substituent having 2 to 6 carbon atoms, R^3 represents a substituent having 1 to 6 carbon atoms, a hydrogen atom or a halogen, M^{n+} represents an alkali metal ion, an alkali earth metal ion, a transition metal ion or an ammonium ion, and n represents an integer of 1 to 4.

3. A polymerizable composition according to Claim 1, wherein said sulfinate initiator component is a sulfinate represented by the general formula



wherein M^{n+} represents Li^+, Na^+, K^+, Mg^{2+} or Ca^{2+}.

4. A polymerizable composition according to claim 1, 2 or 3, wherein the sulfinate initiator component is present in an amount of about 0.01 to about 10% by weight based on the weight of the composition.

5. A polymerizable composition according to any one of claims 1 to 4, wherein said monomer has at least one polymerizable carbon-to-carbon double bond directly linked to an electron attractive group.

6. A polymerizable composition according to any one of claims 1 to 4, wherein said monomer is an acrylate, a methacrylate, an α-haloacrylate, an acrylamide, a methacrylamide, an acrylamide derivative or a methacrylamide derivative.

7. A polymerizable composition according to claim 1 comprising:
(a) said sulfinate initiator component represented by the general formula [I],
(b) a polymerizable monomer, and
(c) an oxidizer,
said (a) and (c) being stored in separate packages and mixed with each other to effect polymerization.

8. A polymerizable composition according to Claim 7, wherein said oxidizer is an organic peroxide.

9. A polymerizable composition according to Claim 7, wherein said oxidizer is an aromatic diacyl peroxide.

10. A polymerizable composition according to Claim 1, comprising:
(a) said sulfinate initiator component represented by the general formula [I],
(b) a polymerizable monomer, and
(c) a photoinitiator.

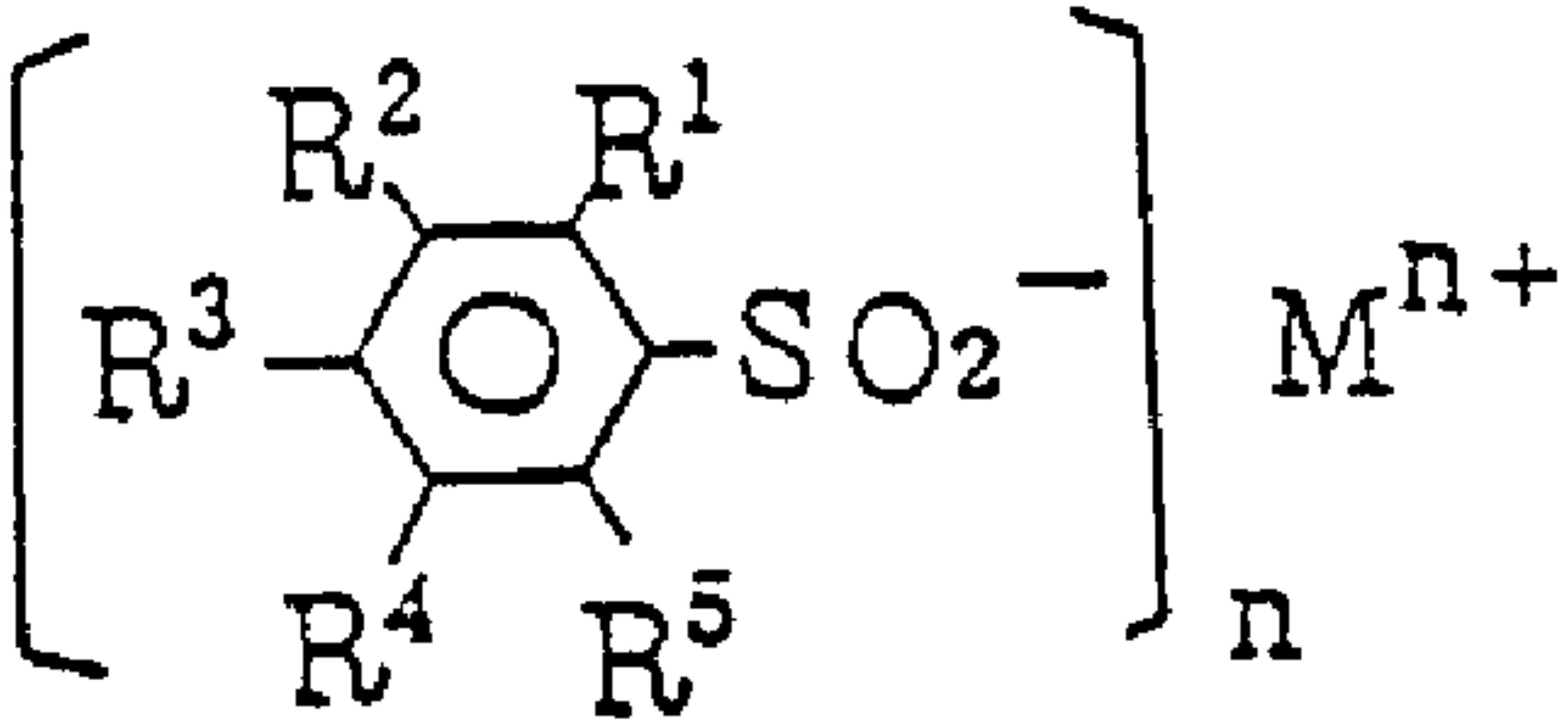
11. A polymerizable composition according to Claim 10, wherein said photoinitiator is a photosensitive dye or an α-diketone.

12. A polymerizable composition according to Claim 1, comprising:
(a) said sulfinate initiator component represented by the general formula [I],
(b) a polymerizable monomer,
(c) an oxidizer, and
(d) an amine,
said oxidizer (c) being stored in a separate package from (a) and (d).

13. A polymerizable composition according to Claim 12, wherein said amine is an aromatic secondary or tertiary amine.

14. A dental adhesive composition comprising the polymerizable composition of any one of claims 1 to 13.

15. Use of the polymerizable composition of any one of claims 1 to 13 in a dental adhesive composition.



[I]