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(72) Inventeurs/Inventors:
RISCHE, THORSTEN, DE;
NAUJOKS, KARIN, DE;
MEIXNER, JURGEN, DE;
FELLER, THOMAS, DE;
KONIG, EBERHARD, DE

(73) Propriétaire/Owner:
BAYER MATERIALSCIENCE AG, DE

(74) Agent: FETHERSTONHAUGH & CO.

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(54) Title: STABILIZED AQUEOUS POLYURETHANE-POLYUREA DISPERSIONS

(57) Abrégé/Abstract:

The invention relates to aqueous polyurethane/polycarbamide dispersions which are stabilised against thermal yellowing, and to the production and use of the same.

ABSTRACT

The invention relates to aqueous polyurethane/polycarbamide dispersions which are stabilised against thermal yellowing, and to the production and use of the same.

Le A 35800

Stabilized aqueous polyurethane-polyurea dispersions

The invention relates to aqueous polyurethane-polyurea dispersions which are stabilized with respect to thermal yellowing, and their preparation and use.

In the coating of substrates, aqueous binders, in particular polyurethane-polyurea (PU) dispersions, are increasingly being used. In some applications, high temperatures which lead to undesired yellowing of the coating are required for drying the coatings.

In the area of sizing of glass fibres, PU dispersions are used as aqueous binders. Owing to the comparatively high temperatures in the coating and drying processes and in the compounding of the sized glass fibres into a plastics matrix, thermal yellowing of the coatings produced often occurs and is undesired.

The prior art discloses numerous stabilizers and additives which can reduce thermal yellowing of binders. The use of these compounds in aqueous systems, such as, for example, PU dispersions, is often possible only to a limited extent. The systems disclosed in the prior art do not adequately meet the needs for protecting an aqueous PU dispersion or the coating resulting therefrom from thermal yellowing.

US-A 5,216,078 discloses a stabilizer which significantly reduces the thermal yellowing of blocked isocyanates, in particular isocyanates blocked with butanone oxime. This compound is a hydrazine adduct.

EP-A 0 829 500 describes a combination of compounds as a stabilizer for blocked polyisocyanates, one of the compounds having at least one 2,2,6,6-tetramethylpiperidinyl radical, the so-called HALS (hindered amine light stabilizer) radical, and the other having a hydrazide structure.

However, the disadvantage of the abovementioned systems is that they are suitable only for solvent-containing finishes and coating and size systems and not for aqueous systems.

The preparation of aqueous PU dispersions is known in principle. The various possibilities for preparing such dispersions was summarized, for example, by D. Dietrich in a review article (D. Dietrich, Prog. Org. Coatings **9**, 281 (1981)). However, the problem of thermal yellowing has not been solved at present in a satisfactory manner in the prior art.

It was therefore the object of the present invention to provide PU dispersions which have been sufficiently stabilized with respect to possible thermal yellowing and moreover are suitable as 1-component or 2-component binders in finishes, sizes and coatings.

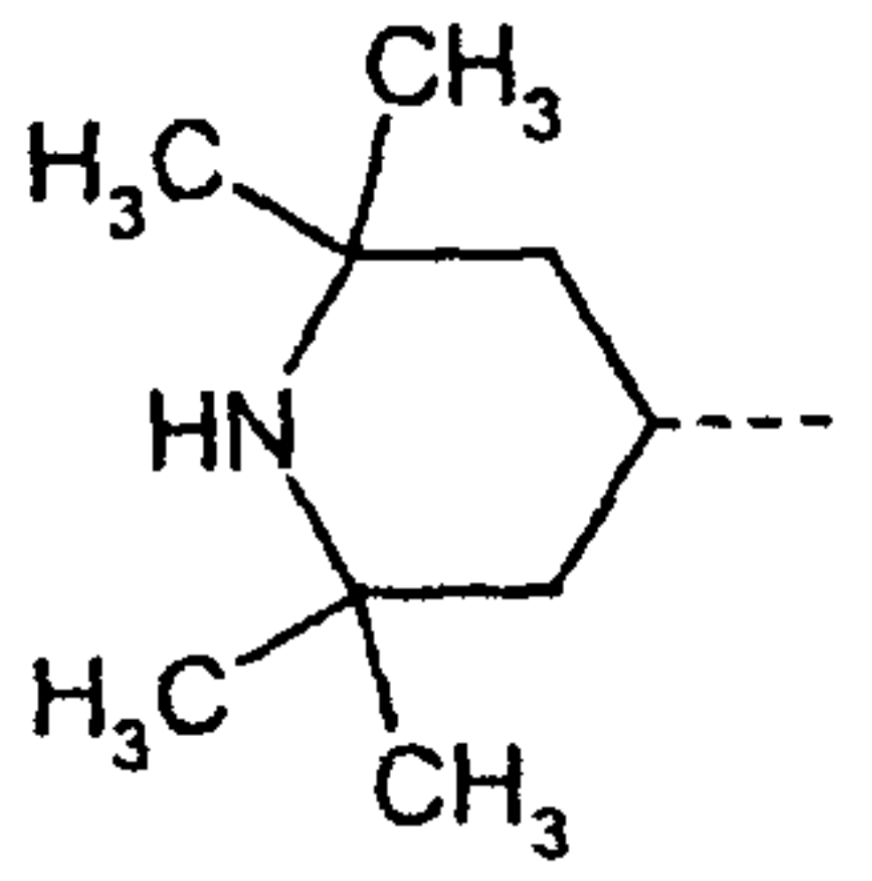
It has now been found that aqueous PU dispersions too can be significantly protected from thermal yellowing by certain combinations of hydrazides and certain sterically hindered amines.

The present invention relates to a binder composition containing

A) at least one aqueous PU dispersion and

B) at least one stabilizer or stabilizer mixture containing

a) at least one amine having the structural unit of the formula (I)



(I)

which has no hydrazide groups,

b) at least one compound having the structural unit of the general formula (II)

-CO-NH-NH- (II)

and

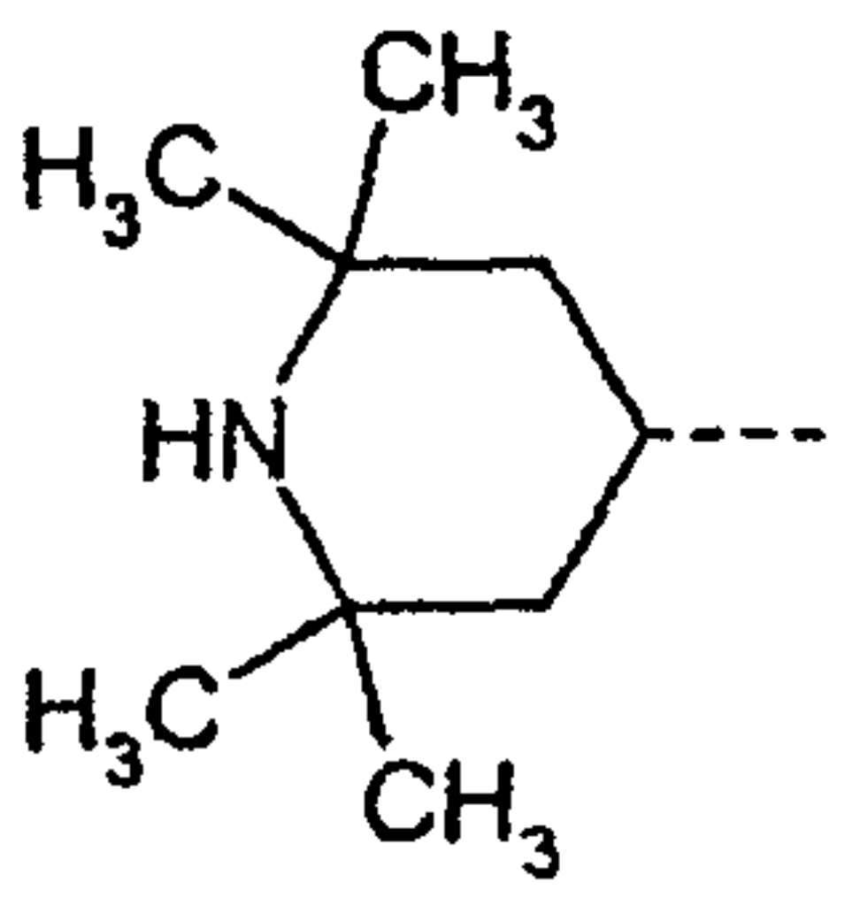
c) optionally a stabilizing component differing from a) and b).

The PU dispersions are prepared in the presence of the components a) and b). It is possible for the components a) and b), depending on the type used, to be incorporated as a structural unit into the polymer skeleton.

The present invention therefore also relates to binder compositions containing

A) at least one aqueous PU dispersion containing structural units or at least one stabilizer or stabilizer mixture B) based on

a) at least one amine of the general formula (I)



(I)

which has no hydrazide groups,

b) at least one compound of the general formula (II)

-CO-NH-NH- (II)

and

c) optionally a stabilizer component differing from a) and b).

The binder composition contains 78.0 to 99.8% by weight, preferably 84.0 to 99.6% by weight, particularly preferably 90.0 to 99.0% by weight, of the component A), and 0.2 to 22.0% by weight, preferably 0.4 to 16.0% by weight, particularly preferably 1.0 to 10.0% by weight, of the component B), the sum of the components always being 100% by weight and forming the total solids content of the binder composition according to the invention.

Based on the total solids content, the binder compositions according to the invention contain 0.1 to 11.0% by weight, preferably 0.2 to 8.0% by weight, particularly preferably 0.5 to 4.0% by weight, of amines having the structural unit of the formula (I) (a), 0.1 to 11.0% by weight, preferably 0.2 to 8.0% by weight, particularly preferably 0.5 to 4.0% by weight, of hydrazides having the structural unit of the formula (II) (b) and optionally 0 to 5.0% by weight of other stabilizers c) differing from a) and b).

In principle, all PU dispersions of the prior art are suitable as component (A). The PU dispersions (A) suitable for the binder composition according to the invention are composed of the components

A1) polyisocyanates

A2) polymeric polyols having average molecular weights of 400 to 6 000,

A3) optionally mono- or polyalcohols or mono- or polyamines,

and at least one compound selected from

A4) compounds which have at least one ionic or potentially ionic group and/or

A5) nonionically hydrophilized compounds.

In the context of the invention, a potentially ionic group is a group which is capable of forming an ionic group.

Preferably, the PU dispersions (A) contain 7 to 45% by weight of A1), 50 to 91% by weight of A2), 0 to 15% by weight of A5), 0 to 12% by weight of ionic or potentially ionic compounds A4) and optionally 0 to 30% by weight of compounds A3), the sum of the components being 100% by weight and it being necessary for the sum of the components A4) and A5) to be not equal to 0.

Particularly preferably, the PU dispersions (A) contain 10 to 30% by weight of A1), 65 to 90% by weight of A2), 0 to 10% by weight of A5), 3 to 9% by weight of ionic or potentially ionic compounds A4) and optionally 0 to 10% by weight of compounds A3), the sum of the components being 100% by weight.

Very particularly preferably, the PU dispersions (A) contain 8 to 27% by weight of A1), 65 to 85% by weight of A2), 0 to 8% by weight of A5), 3 to 8% by weight of ionic or potentially ionic compounds A4) and optionally 0 to 8% by weight of compounds A3), the sum of the components being 100% by weight.

Suitable diisocyanates (A1) are in principle those of the molecular weight range 140 to 400, having aliphatically, cycloaliphatically, araliphatically and/or aromatically bonded isocyanate groups, such as, for example, 1,4-diisocyanatobutane, 1,6-diisocyanatohexane (HDI), 2-methyl-1,5-diisocyanatopentane, 1,5-diisocyanato-2,2-dimethylpentane, 2,2,4- and 2,4,4-trimethyl-1,6-diisocyanatohexane, 1,10-diisocyanatodecane, 1,3- and 1,4-diisocyanatocyclohexane, 1,3- and 1,4-bis-(isocyanatomethyl)-cyclohexane, 1-isocyanato-3,3,5-trimethyl-5-isocyanatomethyl-cyclohexane (isophorone diisocyanate, IPDI), 4,4'-diisocyanatodicyclohexylmethane, 1-isocyanato-1-methyl-4(3)-isocyanatomethylcyclohexane, bis-(isocyanatomethyl)-norbornane, 1,3- and 1,4-bis-(2-isocyanato-prop-2-yl)-benzene (TMXDI), 2,4- and 2,6-diisocyanatotoluene (TDI), 2,4'- and 4,4'-diisocyanatodiphenylmethane, 1,5-diisocyanatonaphthalene or any desired mixtures of such diisocyanates.

They are preferably polyisocyanates or polyisocyanate mixtures of said type having exclusively aliphatically and/or cycloaliphatically bonded isocyanate groups. Very particularly preferred starting components (A1) are polyisocyanates and polyisocyanate mixtures based on HDI, IPDI and/or 4,4'-diisocyanatodicyclohexylmethane.

Any desired polyisocyanates prepared by modification of simple aliphatic, cycloaliphatic, araliphatic and/or aromatic diisocyanates, composed of at least two diisocyanates and having a uretdione, isocyanurate, urethane, allophanate, biuret, iminooxadiazinedione and/or oxadiazinetrione structure, as described, for example, in J. Prakt. Chem. 336 (1994), pages 185 - 200, are furthermore suitable as polyisocyanates (A1).

The polymeric polyols (A2) in the molecular weight range of 400 to 6 000 are the customary ones as have long been used for polyurethane and have an OH functionality of at least 1.8 to 4, such as, for example, polyacrylates, polyesters, polylactones, polyethers, polycarbonates, polyestercarbonates, polyacetals, polyolefins and polysiloxanes. Polyols in a molecular weight range of from 600 to 2 500 and having an OH functionality of 2 to 3 are preferred.

The suitable polycarbonates having hydroxyl groups are obtainable by reacting carbonic acid derivatives, e.g. diphenyl carbonate, dimethyl carbonate or phosgene, with diols. Suitable such diols are, for example, ethylene glycol, 1,2- and 1,3-propanediol, 1,3- and 1,4-butanediol, 1,6-hexanediol, 1,8-octanediol, neopentylglycol, 1,4-bishydroxymethylcyclohexane, 2-methyl-1,3-propanediol, 2,2,4-trimethyl-1,3-pentanediol, dipropylene glycol, polypropylene glycols, dibutylene glycol, polybutylene glycols, bisphenol A, tetrabromobisphenol A and lactone-modified diols. The diol component preferably contains 40 to 100% by weight of hexanediol, preferably 1,6-hexanediol, and/or hexanediol derivatives, preferably those which have ether or ester groups in addition to terminal OH groups, e.g. products which were obtained by reacting 1 mol of hexanediol with at least 1 mol, preferably 1 to 2 mol, of caprolactone according to DE-A 17 70 245 or by etherifying hexanediol with itself to give di- or trihexylene glycol. The preparation of such derivatives is disclosed, for example, in DE-A 15 70 540. The polyether-polycarbonatediols described in DE-A 37 17 060 can also be used.

The hydroxypolycarbonates should be substantially linear. However, they may optionally be slightly branched by incorporation of polyfunctional components, in particular low molecular weight polyols. For example, glycerol, trimethylolpropane, 1,2,6-hexanetriol, 1,2,4-butanetriol, trimethylolpropane, pentaerythritol, quinitol, mannitol and sorbitol, methylglycoside and 1,3,4,6-dianhydrohexitols are suitable for this purpose.

Suitable polyetherpolyols are the polytetramethylene glycol polyethers which are known per se in polyurethane chemistry and can be prepared, for example, via polymerization of tetrahydrofuran by cationic ring cleavage.

Other suitable polyetherpolyols are polyether, such as, for example, the polyols prepared using initiator molecules, from styrene oxide, propylene oxide, butylene oxides or epichlorohydrins, in particular of propylene oxide.

Suitable polyesterpolyols are, for example, reaction products of polyhydric, preferably dihydric and optionally additionally trihydric, alcohols with polybasic, preferably dibasic, carboxylic acids. Instead of the free polycarboxylic acids, it is also possible to use corresponding polycarboxylic anhydrides or corresponding polycarboxylic esters of lower alcohols or their mixtures for the preparation of the polyester. The polycarboxylic acids may be aliphatic, cycloaliphatic, aromatic and/or heterocyclic and optionally substituted, for example by halogen atoms, and/or unsaturated.

Monofunctional alcohols and monoamines are suitable for the components (A3) suitable for terminating the polyurethane prepolymer. Preferred monoalcohols are aliphatic monoalcohols having 1 to 18 C atoms, such as, for example, ethanol, n-butanol, ethylene glycol monobutyl ether, 2-ethylhexanol, 1-octanol, 1-dodecanol or 1-hexadecanol. Preferred monoamines are aliphatic monoamines, such as, for example, diethylamine, dibutylamine, ethanolamine, N-methylethanolamine or N,N-diethanolamine.

The polyols, aminopolyols or polyamines having a molecular weight of less than 400, which are described in large numbers in the corresponding literature, are also suitable as component (A3).

Examples of preferred components (A3) are:

a) Alkanediols, such as ethanediol, 1,2- and 1,3-propanediol, 1,4- and 2,3-butanediol, 1,5-pentanediol, 1,3-dimethylpropanediol, 1,6-hexanediol, neopentylglycol, cyclohexanedimethanol and 2-methyl-1,3-propanediol,

b) etherdiols, such as diethylene diglycol, triethylene glycol or hydroquinone dihydroxyethyl ether,

c) esterdiols of the general formulae (III) and (IV)

$$HO\text{-}(CH_2)_x\text{-}CO\text{-}O\text{-}(CH_2)_y\text{-}OH \qquad (III)$$

$$HO\text{-}(CH_2)_x\text{-}O\text{-}CO\text{-}R\text{-}CO\text{-}O(CH_2)_x\text{-}OH \qquad (IV)$$

in which

R is an alkylene or arylene radical having 1 to 10 C atoms, preferably 2 to 6 C atoms,

x is 2 to 6 and

y is 3 to 5,

such as, for example, α-hydroxybutyl ε-hydroxycaproate, ω-hydroxyhexyl γ-hydroxybutyrate, ß-hydroxyethyl adipate and bis(ß-hydroxy-ethyl) terephthalate, and

d) polyamines, such as ethylenediamine, 1,2- and 1,3-diaminopropane, 1,4-diaminobutane, 1,6-diaminohexane, isophoronediamine, isomer mixture of 2,2,4- and 2,4,4-trimethylhexa-methylenediamine, 2-methylpentamethylenediamine, diethylene-triamine, 1,3- and 1,4-xylylenediamine, α,α,α',α'-tetramethyl-1,3- and -1,4-xylylenediamine and 4,4-diaminodicyclohexylmethane. Suitable diamines in the context of the invention are also hydrazine, hydrazine hydrate and substituted hydrazines, such as, for example, N-methylhydrazine, N,N'-dimethylhydrazine and their homologs and acid dihydrazides, adipic acid, ß-methyladipic acid, sebacic acid, hydracrylic acid and terephthalic acid, semicarbazidoalkylene hydrazides, such as, for example, ß-semicarbazidopropionic acid hydrazide (e.g. DE-A 17 70 591), semicarbazidoalkylene-carbazine esters, such as, for example, 2-semicarbazidoethylcarbazine ester (e.g. DE-A 19 18 504), or aminosemicarbazide compounds, such as, for example, ß-aminoethyl semicarbazido-carbonate (e.g. DE-A 19 02 931).

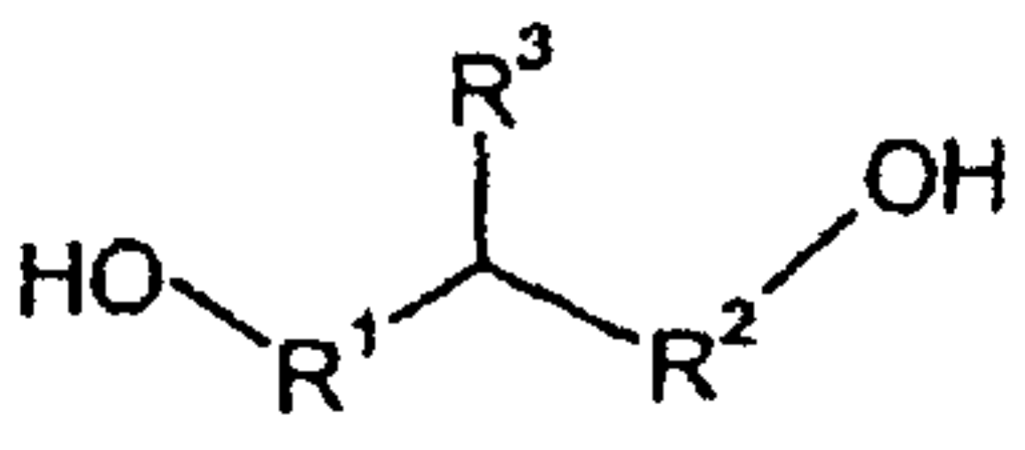
Suitable ionic or potentially ionic compounds (A4) are, for example, mono- and dihydroxycarboxylic acids, mono- and diaminocarboxylic acids, mono- and dihydroxysulphonic acids, mono- and diaminosulphonic acids and mono- and dihydroxyphosphonic acids or mono- and diaminophosphonic acids and their salts, such as dimethylolpropionic acid, hydroxypivalic acid, N-(2-aminoethyl)-ß-alanine, 2-(2-amino-ethylamino)-ethanesulphonic acid, ethylenediamine-propanesulphonic or ethylenediamine-butanesulphonic acid, 1,2- or 1,3-propylenediamine-ß-ethylsulphonic acid, lysine or 3,5-diaminobenzoic acid. The hydrophilizing agent according to Example 1 of EP-A 0 916 647 and its alkali metal and/or ammonium salts are also suitable. The adduct of sodium bisulphite with but-2-ene-1,4-diol, polyethersulphonate, the propoxylated adduct of 2-butenediol and $NaHSO_3$ (e.g. in DE-A 24 46 440, pages 5-9) and building blocks, such as N-methyldiethanolamine, which can be converted into cationic groups can be used as hydrophilic components. Preferred ionic or potentially ionic compounds (A4) are those which have carboxyl and/or carboxylate and/or sulphonate groups and/or ammonium groups. Particularly preferred ionic compounds (A4) are those which contain carboxylate and/or sulphonate groups as ionic or potentially ionic groups, such as the salts of

N-(2-aminoethyl)-ß-alanine, 2-(2-aminoethylamino)ethanesulphonic acid or of the hydrophilizing agent according to Example 1 of EP-A 0 916 647 and of dimethylolpropionic acid.

Preferably, the PU dispersions (A) contain a combination of nonionic and ionic hydrophilizing agents. Combinations of nonionic and anionic hydrophilizing agents are particularly preferred.

The hydroxy components among components (A2), (A3) and (A4) may contain double bonds which may originate, for example, from long-chain aliphatic carboxylic acids or fatty alcohols. Functionalization with olefinic double bonds is possible, for example, by the incorporation of allylic groups or of acrylic acid or methacrylic acid and their respective esters.

Furthermore, the polyurethane dispersions (A) may contain nonionically hydrophilic compounds (A5), e.g. polyoxyalkylene ethers having at least one hydroxyl or amino group. These polyethers contain a proportion of 30% by weight to 100% by weight of building blocks which are derived from ethylene oxide. Linear polyethers having a functionality between 1 and 3, but also compounds of the general formula (V)



(V)

in which

R^1 and R^2,	independently of one another, each denote a divalent aliphatic, cycloaliphatic or aromatic radical having 1 to 18 C atoms which may be interrupted by oxygen and/or nitrogen atoms and
R^3	represents a non-hydroxyl-terminated polyester or preferably polyether. R^3 particularly preferably represents an alkoxy-terminated polyethylene oxide radical,

are suitable.

The preparation of the aqueous polyurethane dispersions (A) is carried out in the manner known from the prior art. The polyisocyanate components with polymeric polyol and low molecular weight chain extenders is reacted to give a polyurethane, a solvent, which can be separated off again later, optionally being concomitantly used. Suitable solvents are the customary coating solvents known per se, such as, for example, ethyl acetate, butyl acetate, 1-methoxyprop-2-yl acetate, 3-methoxy-n-butyl acetate, acetone, 2-butanone, 4-methyl-2-pentanone, cyclohexanone, toluene, xylene, chlorobenzene, mineral spirit, mixtures which contain in particular relatively highly substituted aromatics as are commercially available, for example, under the names Solvent Naphtha, Solvesso® (Exxon Chemicals, Houston, USA), Cypar® (Shell Chemicals, Eschborn, DE), Cyclo Sol® (Shell Chemicals, Eschborn, DE), Tolu Sol® (Shell Chemicals, Eschborn, DE), Shellsol® (Shell Chemicals, Eschborn, DE), carbonic acid esters, such as dimethyl carbonate, diethyl carbonate, 1,2-ethylene carbonate and 1,2-propylene carbonate, lactones, such as ß-propiolactone, γ-butyrolactone, ε-caprolactone and ε-methylcaprolactone, propylene glycol diacetate, diethylene glycol dimethyl ether, dipropylene glycol dimethyl ether, diethylene glycol ethyl and butyl ether acetate, N-methylpyrrolidone and N-methylcaprolactam, or any desired mixtures of such solvents. Preferred solvents are acetone, 2-butanone and N-methylpyrrolidone. Acetone is particularly preferred.

In a further step, groups capable of neutralization are then optionally converted into the salt form and transferred to the aqueous phase. Depending on the degree of neutralization and content of ionic groups, the dispersion may be made very finely divided so that it virtually has the appearance of a solution, but very coarse-particled formulations are also possible and are likewise sufficiently stable.

However, the mean particle sizes of less than 300 nm are preferred since these improve the emulsification of a polyisocyanate and hence the quality of the coating film. The solids content may be varied within limits from 10 to 70% by weight.

The binder compositions according to the invention are preferably composed of PU dispersions (A) which have been prepared by the acetone process known from the literature.

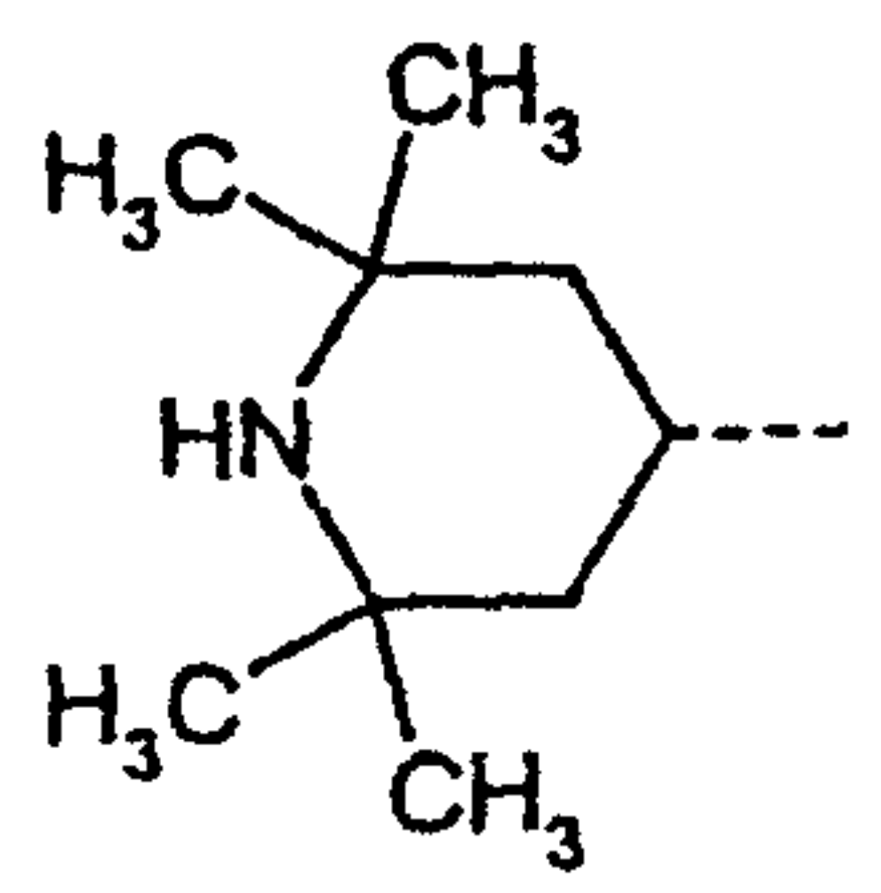
Excess isocyanate groups can then be reacted by reaction with polyfunctional isocyanate-reactive compounds (A3). Water or the polyamines already mentioned under (A3), particularly preferably di- and triamines, hydrazine and the sodium salt of 2-(2-amino-ethylamino)-ethanesulphonic acid, are preferably used for this purpose. Termination with a monoamine, such as, for example, diethylamine, dibutylamine, ethanolamine, N-methylethanolamine or N,N-diethanolamine is also possible.

Optionally used solvents can then be removed by distillation.

It is furthermore possible to modify the binder compositions according to the invention by means of polyacrylates. For this purpose, an emulsion polymerization of olefinically unsaturated monomers, for example esters of (meth)acrylic acid and alcohols having 1 to 18 C atoms, styrene, vinyl esters or butadiene, is carried out in the presence of the polyurethane dispersion (A), as described, for example, in DE-A 19 53 348, EP-A 0 167 188, EP-A 0 189 945 and EP-A 0 308 115.

In addition to one or more olefinic double bonds, the monomers may also contain functional groups, such as hydroxyl, epoxy, methylol or acetoacetoxy groups. The emulsion polymerization can be carried out before or after the modification with component (B).

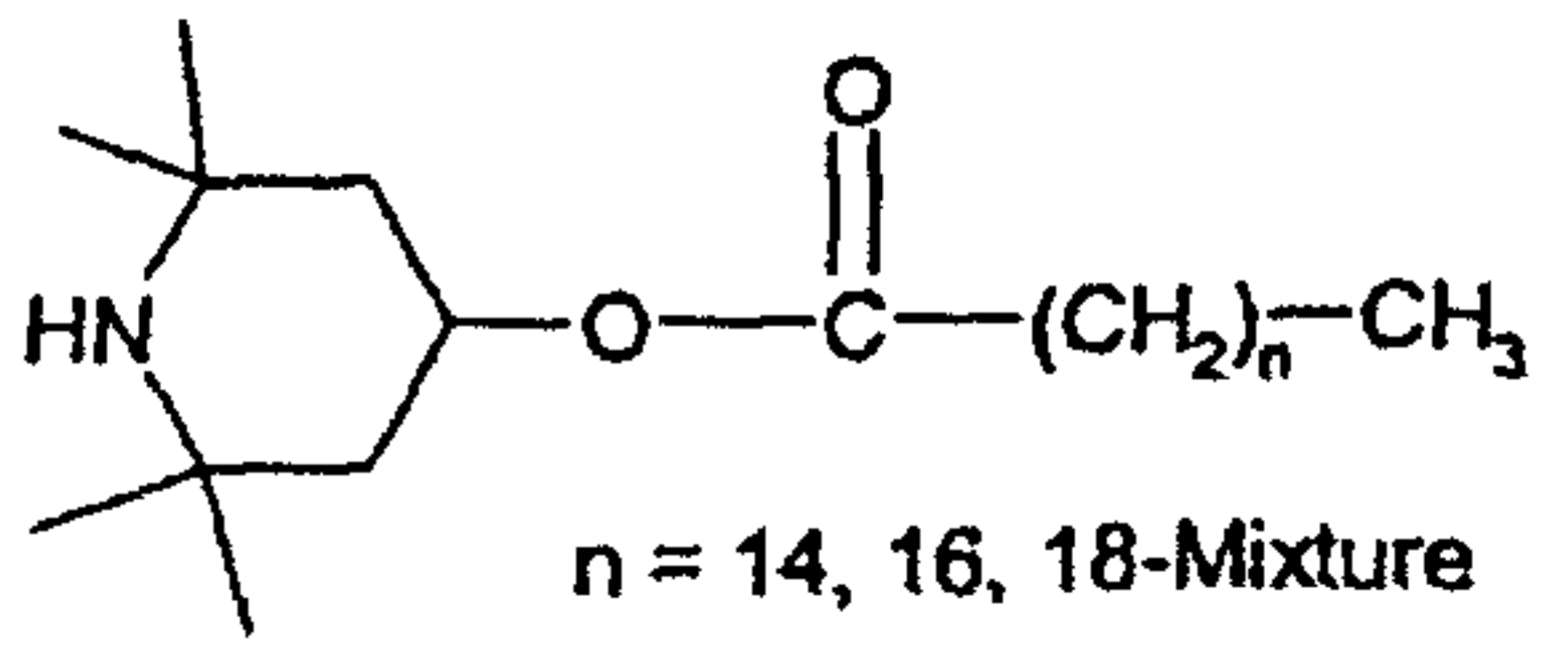
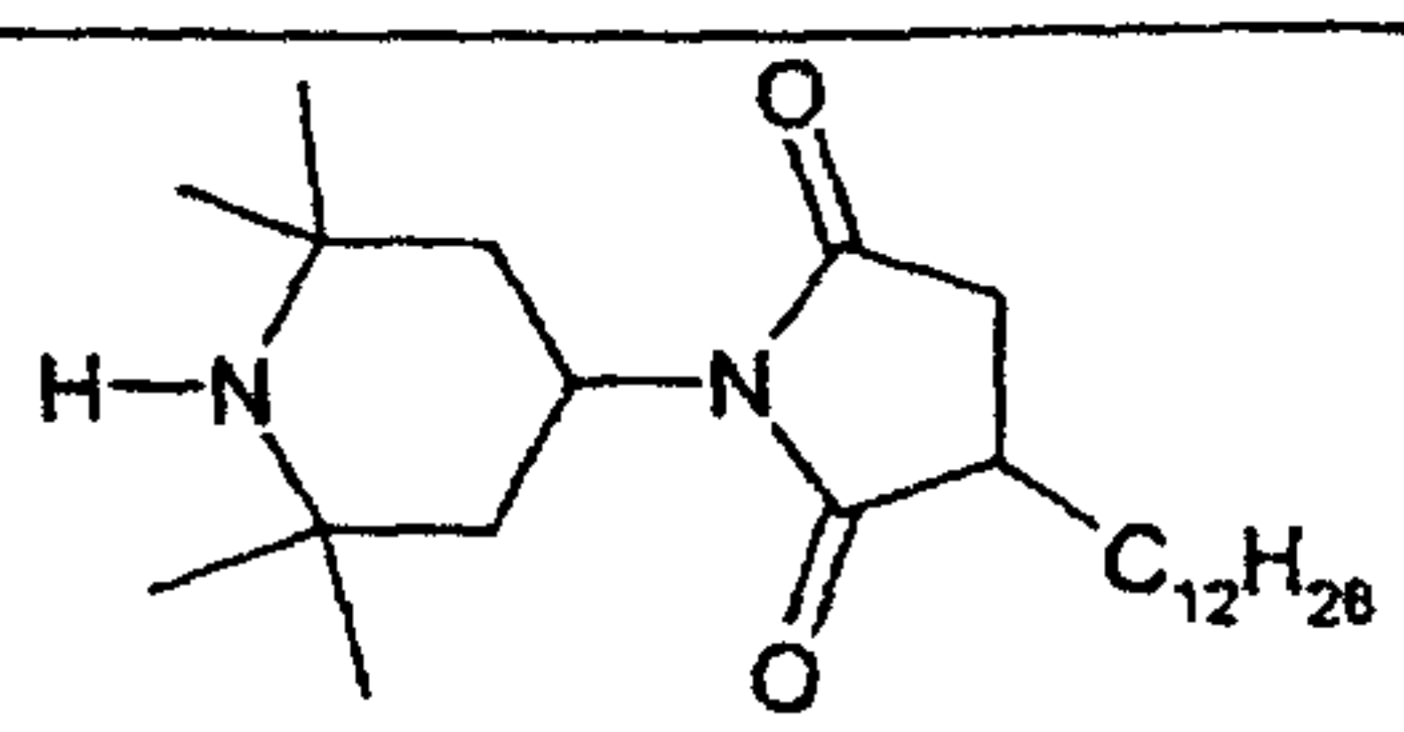
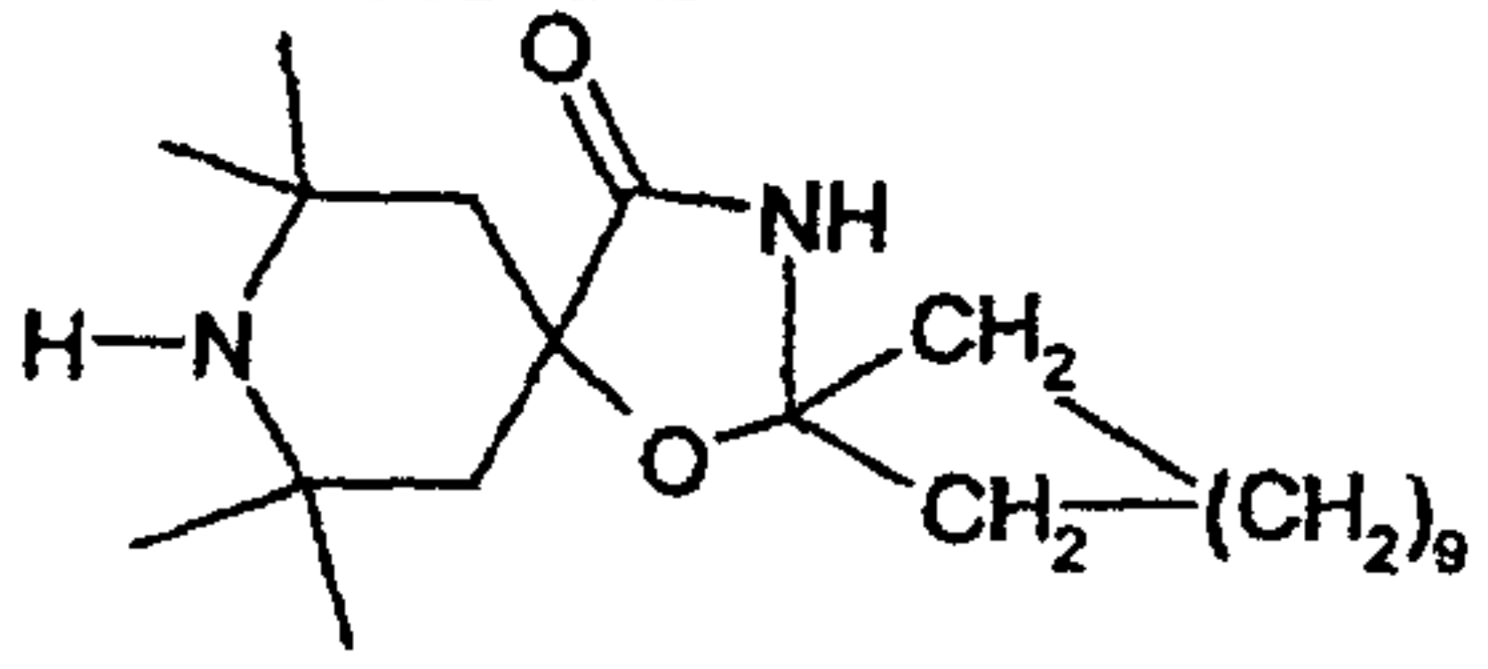
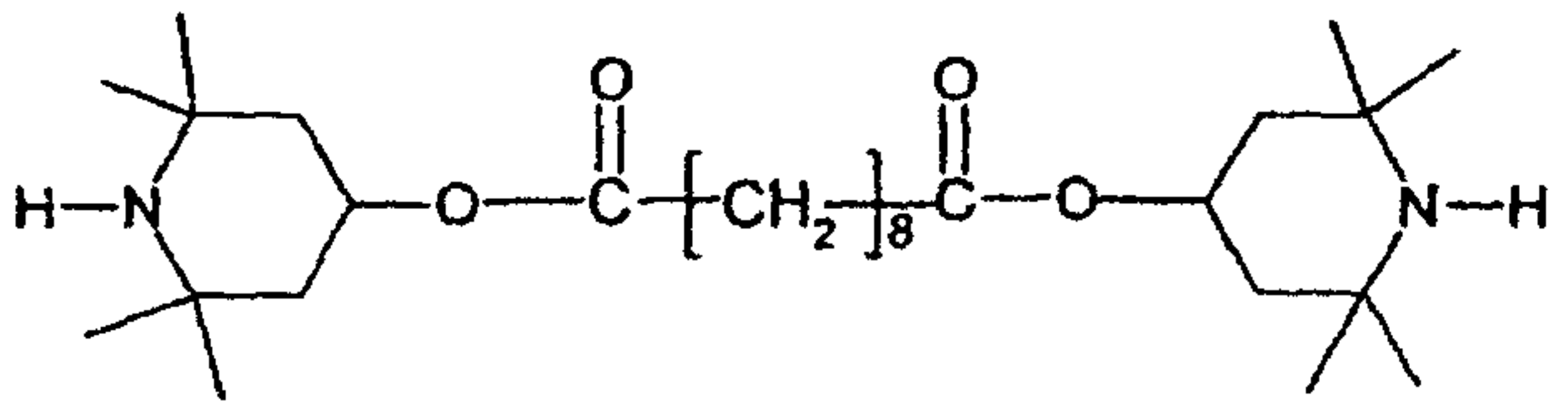
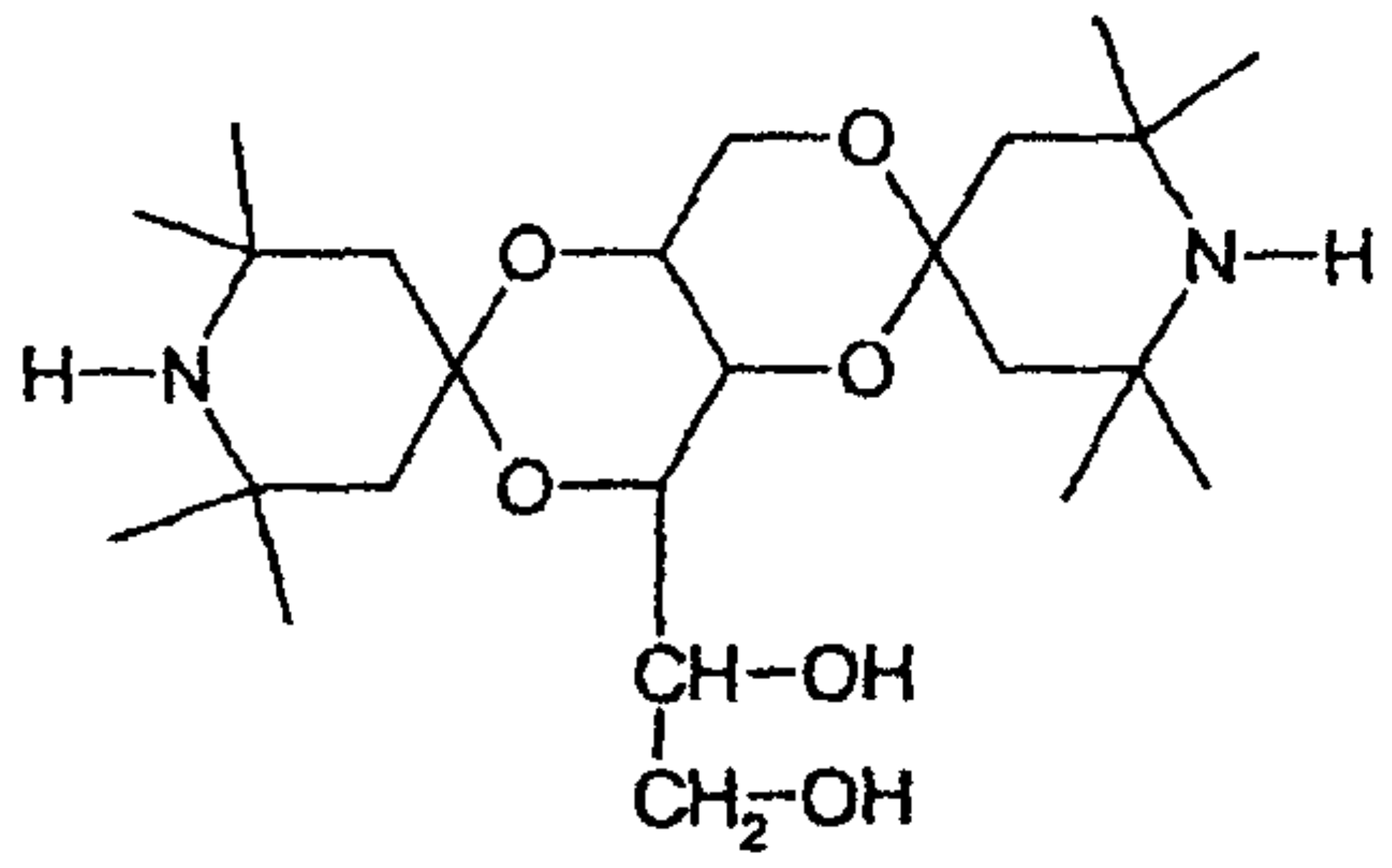
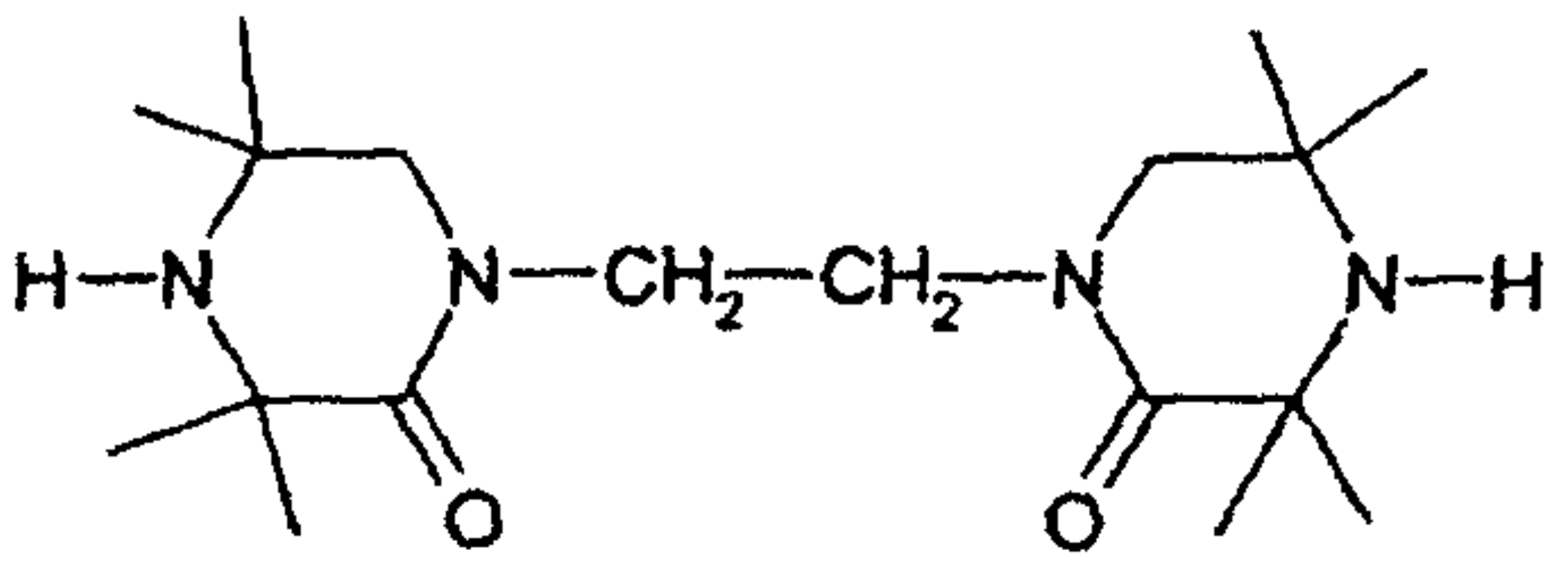
The compositions according to the invention contain a stabilizer mixture B) which contains a) an amine having the structural unit of the general formula (I)

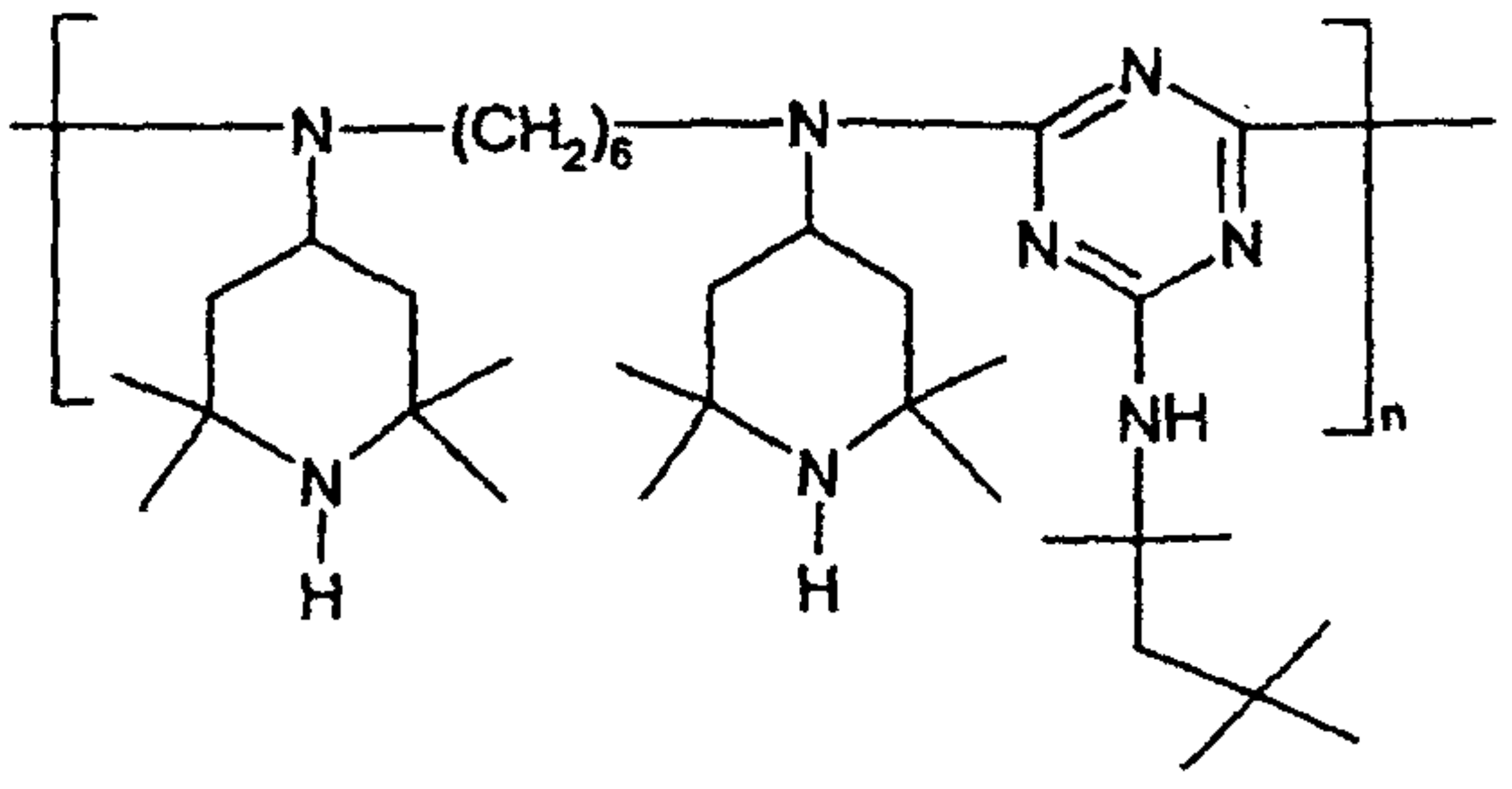
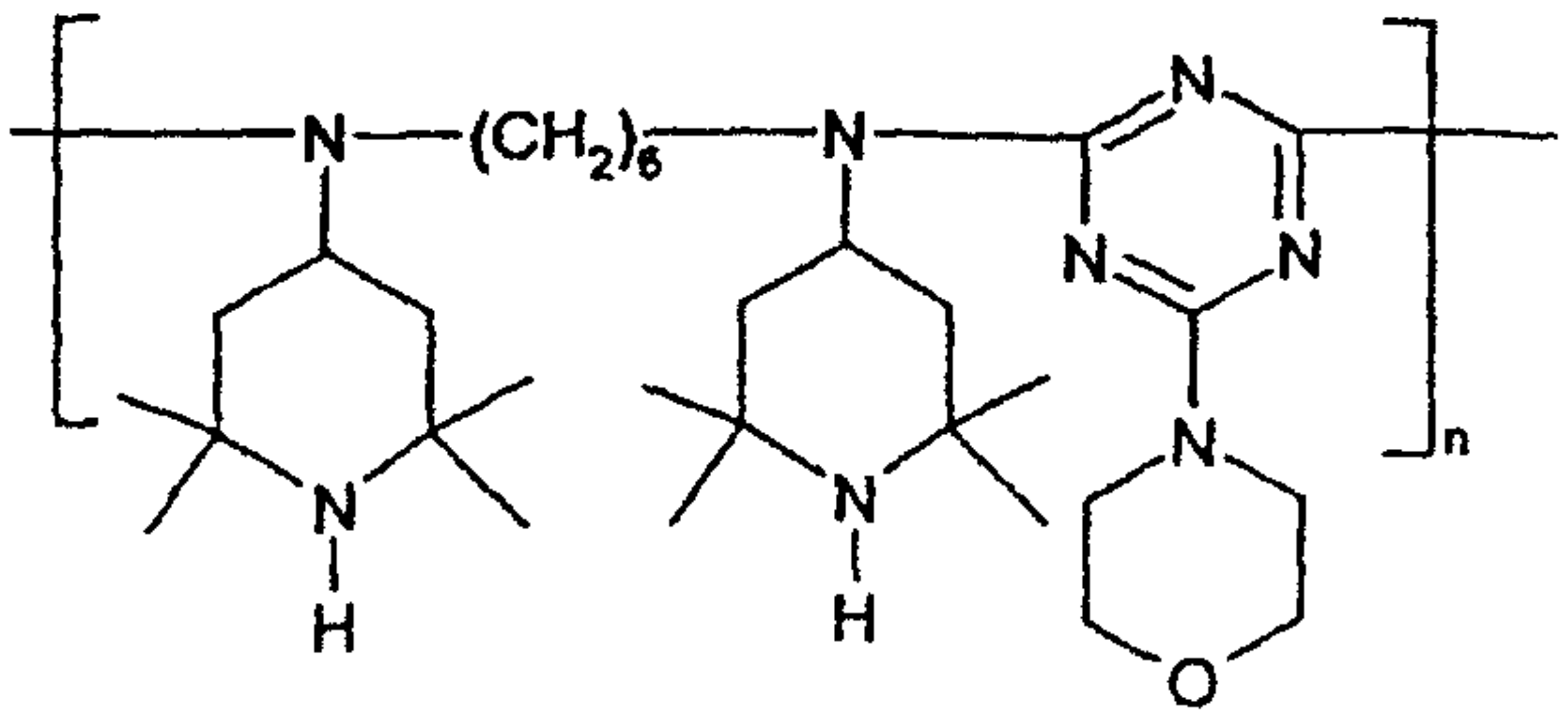
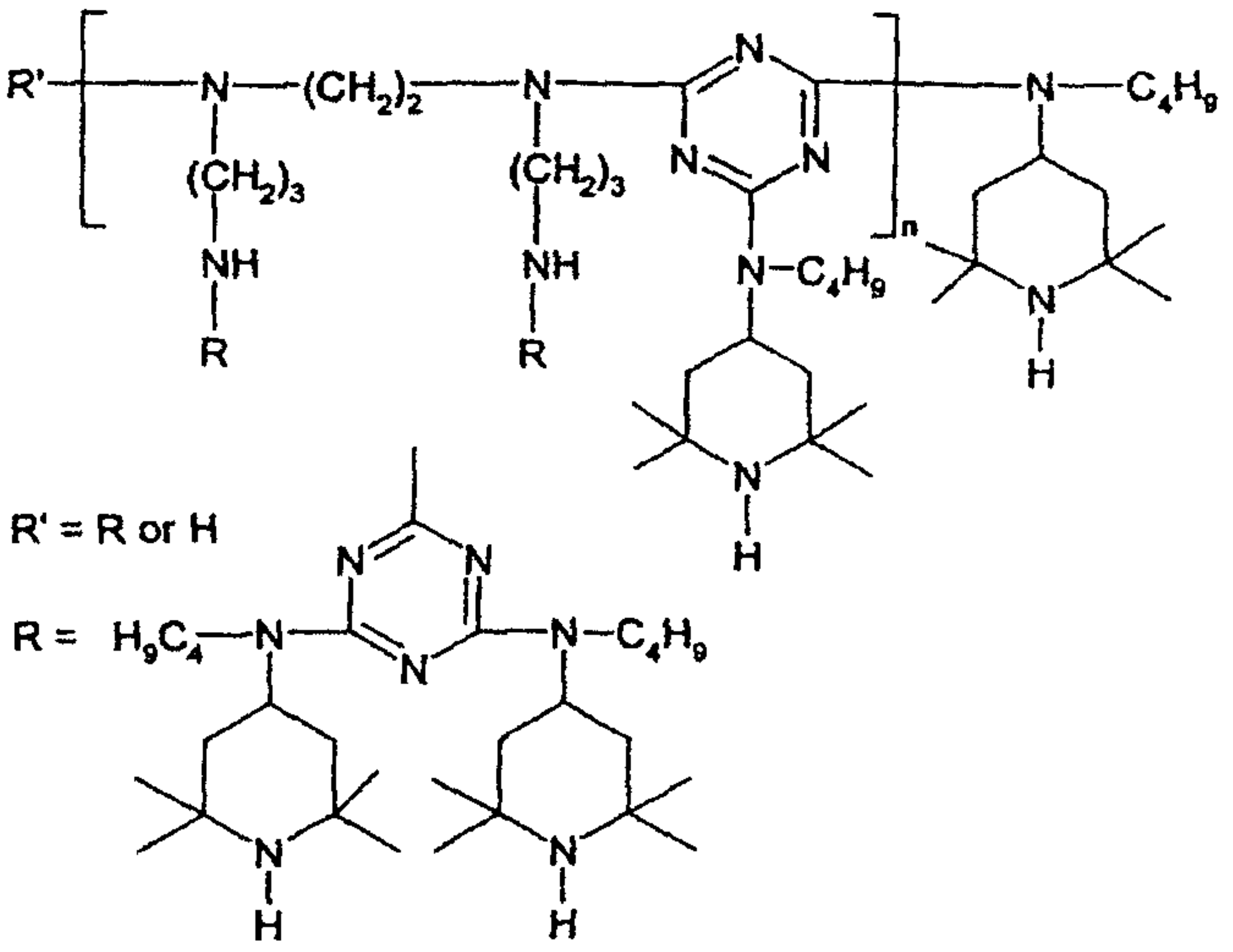
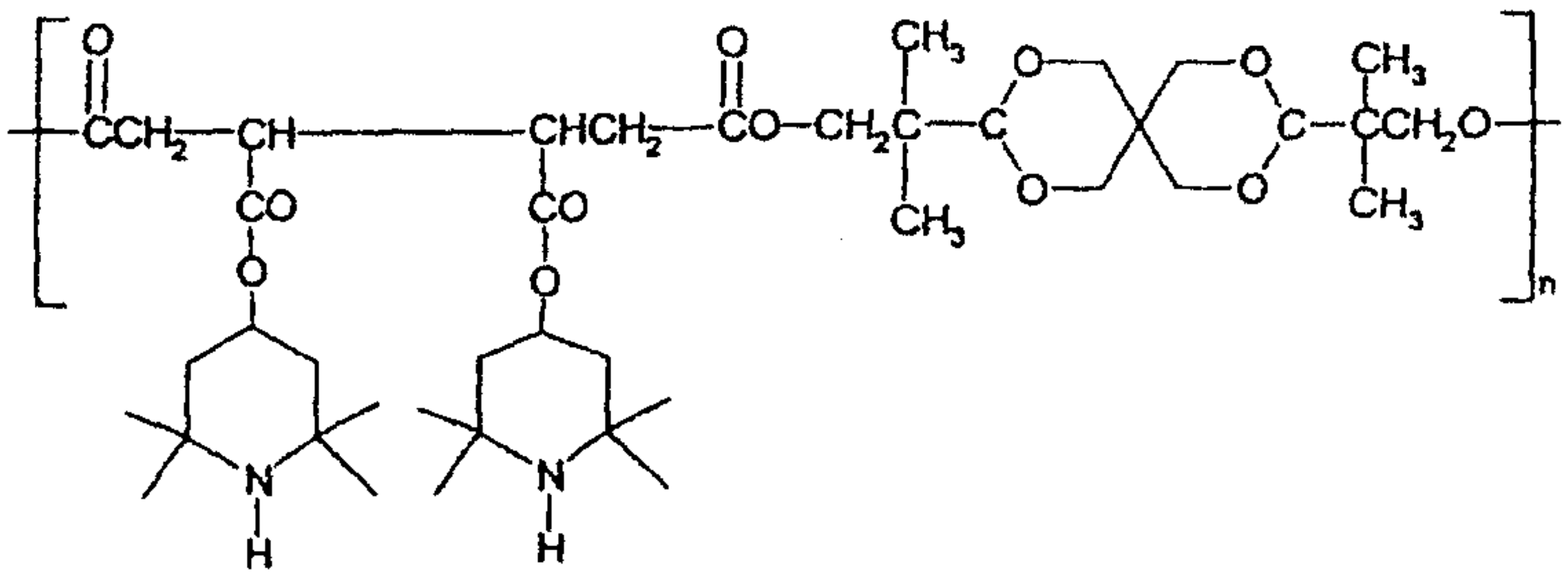


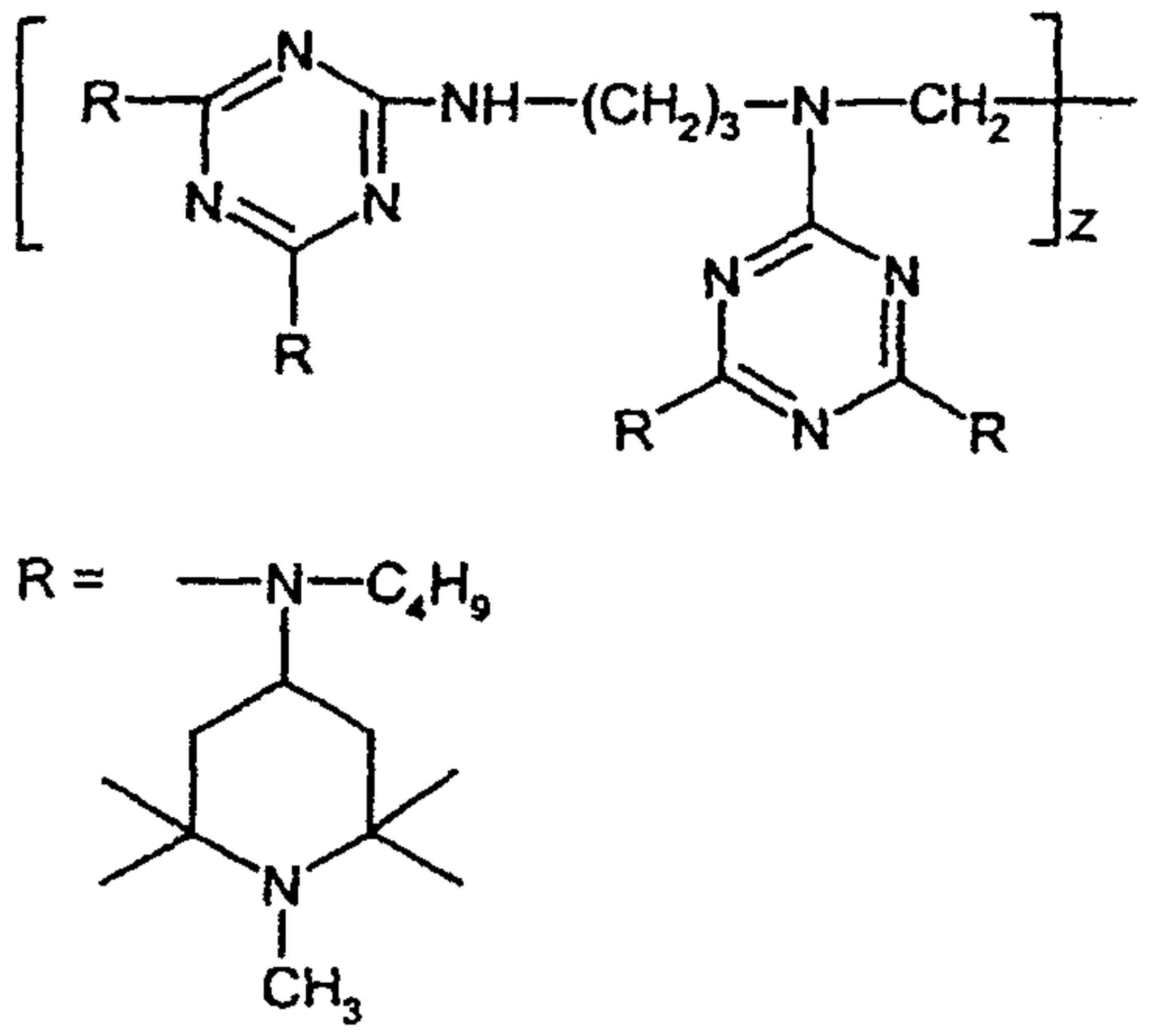
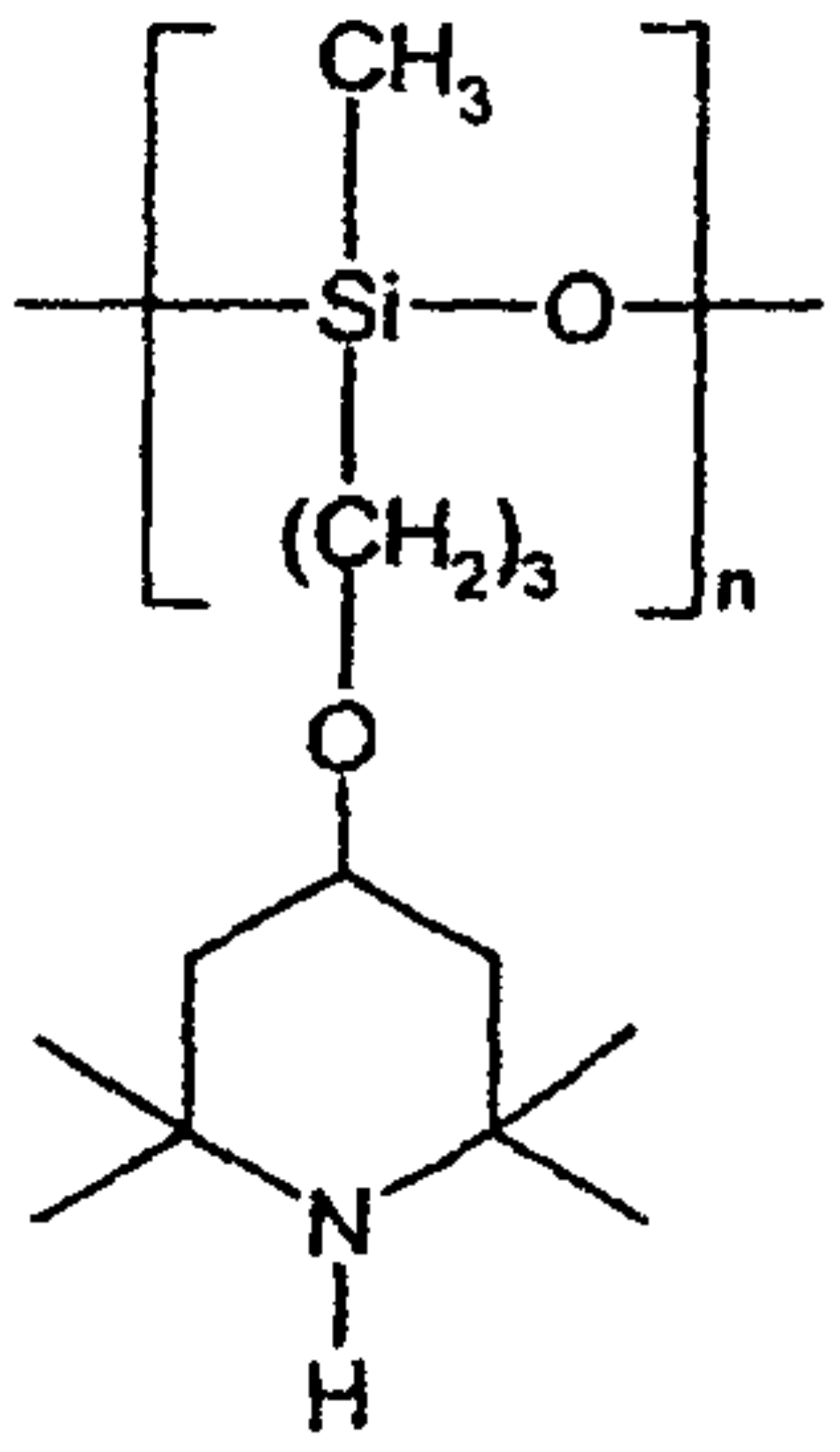
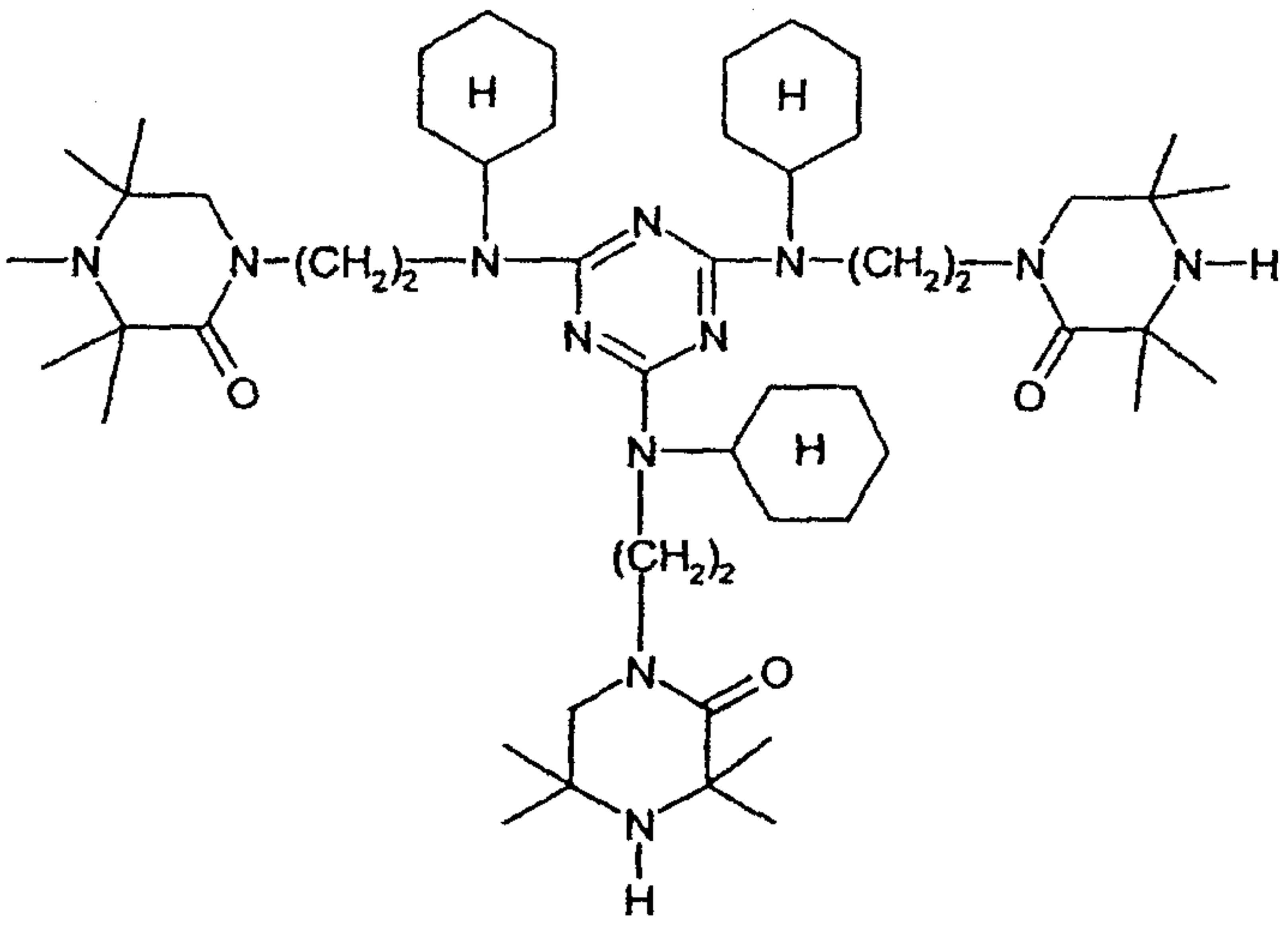
(I)

Suitable compounds a) are those which have a 2,2,6,6-tetramethylpiperidinyl radical (HALS ring). The piperidinyl nitrogen of the HALS ring is not substituted and has no hydrazide structures at all. Preferred compounds a) are the compounds shown in Table 1.

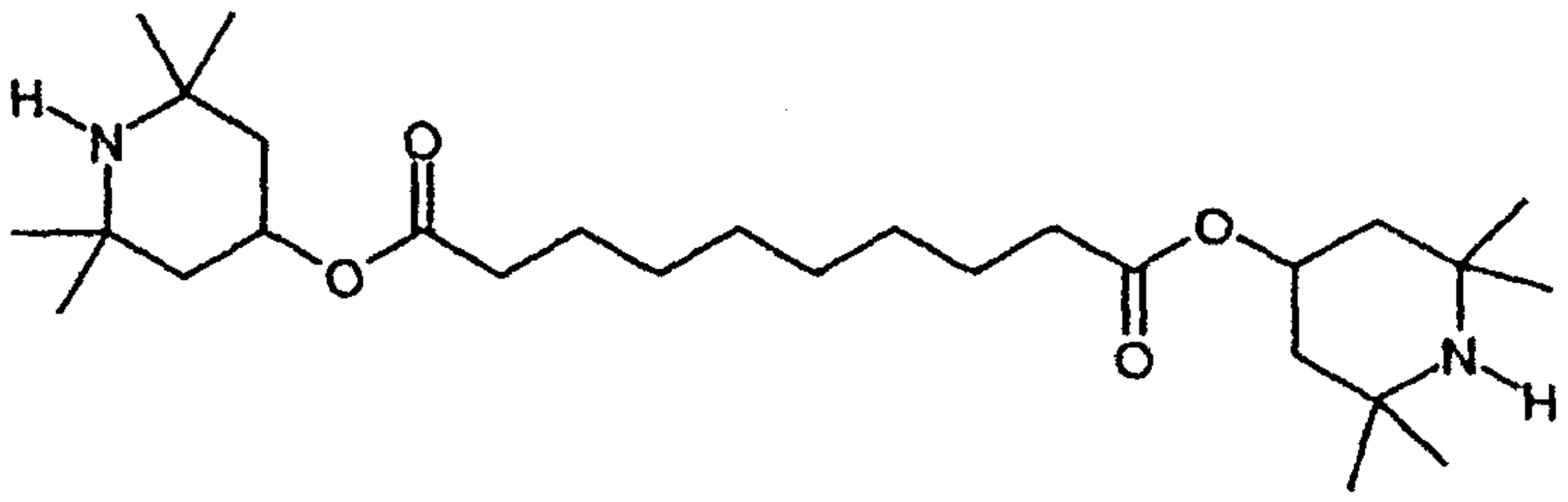
Table 1: Compounds a)

CAS Reg. No.	Structure
24860-22-8	 n = 14, 16, 18-Mixture
79720-19-7	
64338-16-5	
52829-07-9	
99473-08-2	
71029-16-8	

CAS Reg. No.	Structure
71878-19-8	
90751-07-8	
154636-38-1	
100631-44-5	

CAS Reg. No.	Structure
115810-23-6	
164648-93-5	
96204-36-3	

A compound of the formula (VI), which is sold, for example, under the name Tinuvin® 770 DF by Ciba Spezialitäten (Lampertheim, DE), is particularly preferred:

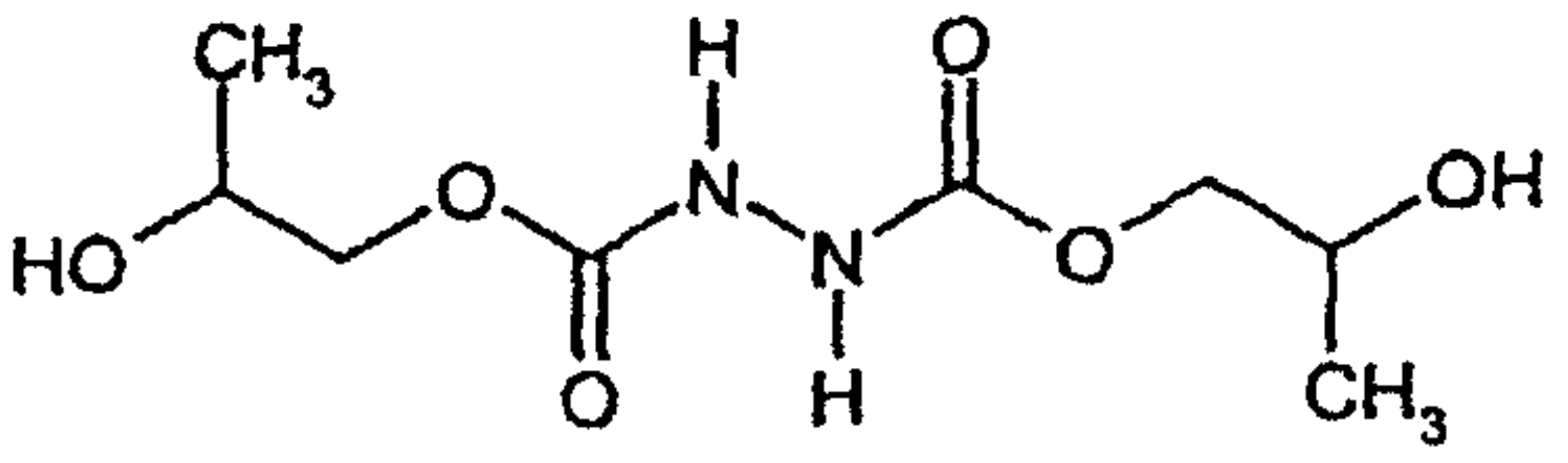


(VI)

The stabilizer B) of the compositions according to the invention likewise contains a compound b) of the general formula (II)

-CO-NH-NH- (II).

Suitable compounds b) are, for example, acid hydrazides and acid dihydrazides, such as, for example, acetic acid hydrazide, adipic acid hydrazide or adipic acid dihydrazide, or hydrazine adducts of hydrazine and cyclic carbonates, as mentioned, for example, in EP-A 654 490 (page 3, line 48 to page 4, line 3). Adipic acid dihydrazide or an adduct of 2 mol of propylene carbonate and 1 mol of hydrazine, of the general formula (VII)



(VII)

is preferably used. The adduct of 2 mol of propylene carbonate and 1 mol of hydrazine, of the general formula (VII), is particularly preferred.

Suitable compounds c) are, for example, antioxidants, such as 2,6-di-tert-butyl-4-methylphenol, UV absorbers of the 2-hydroxyphenyl-benzotriazole type or light stabilizers of the type consisting of the HALS compounds substituted on the nitrogen atom, such as Tinuvin® 292 (Ciba Spezialitäten GmbH, Lampertheim, DE), or other commercially available stabilizers, as described, for example, in "Lichtschutzmittel für Lacke" [Light stabilizers for finishes] (A. Valet, Vincentz Verlag, Hanover, 1996, and "Stabilization of Polymeric Materials" (H. Zweifel, Springer Verlag, Berlin, 1997, Appendix 3, pages 181-213). Preferred compounds c) are shown in Table 2.

Table 2: Compounds c)

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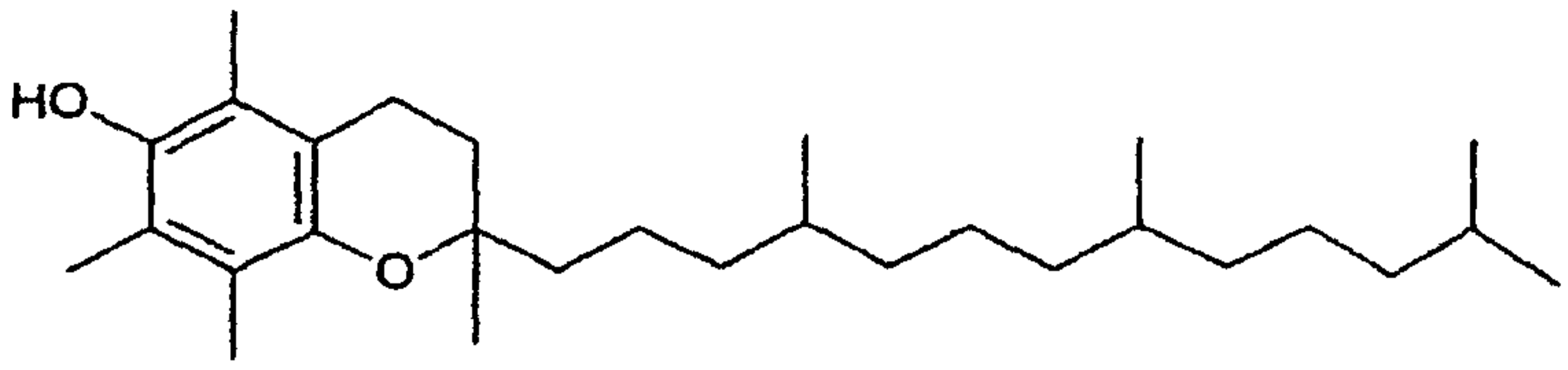
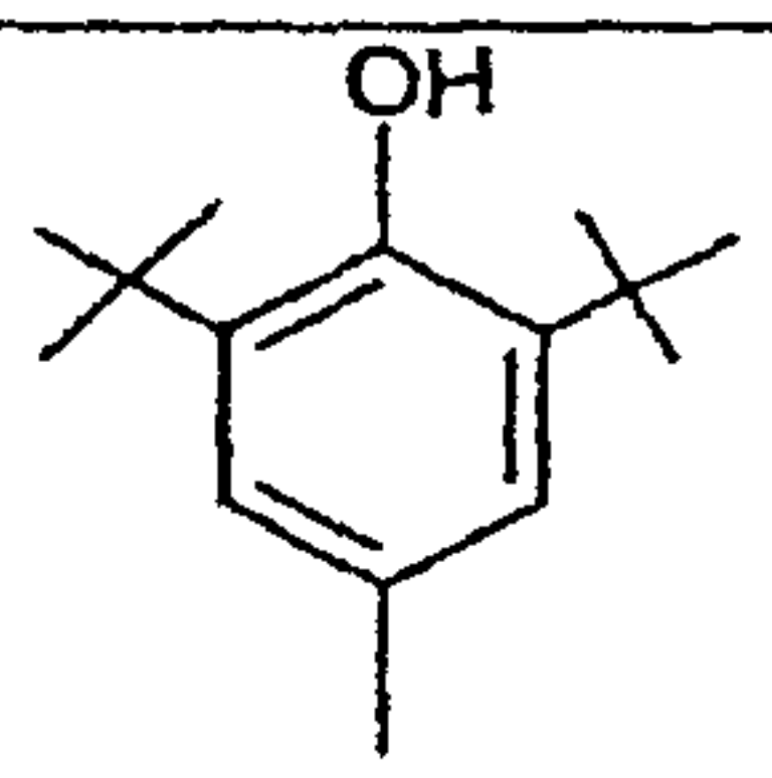
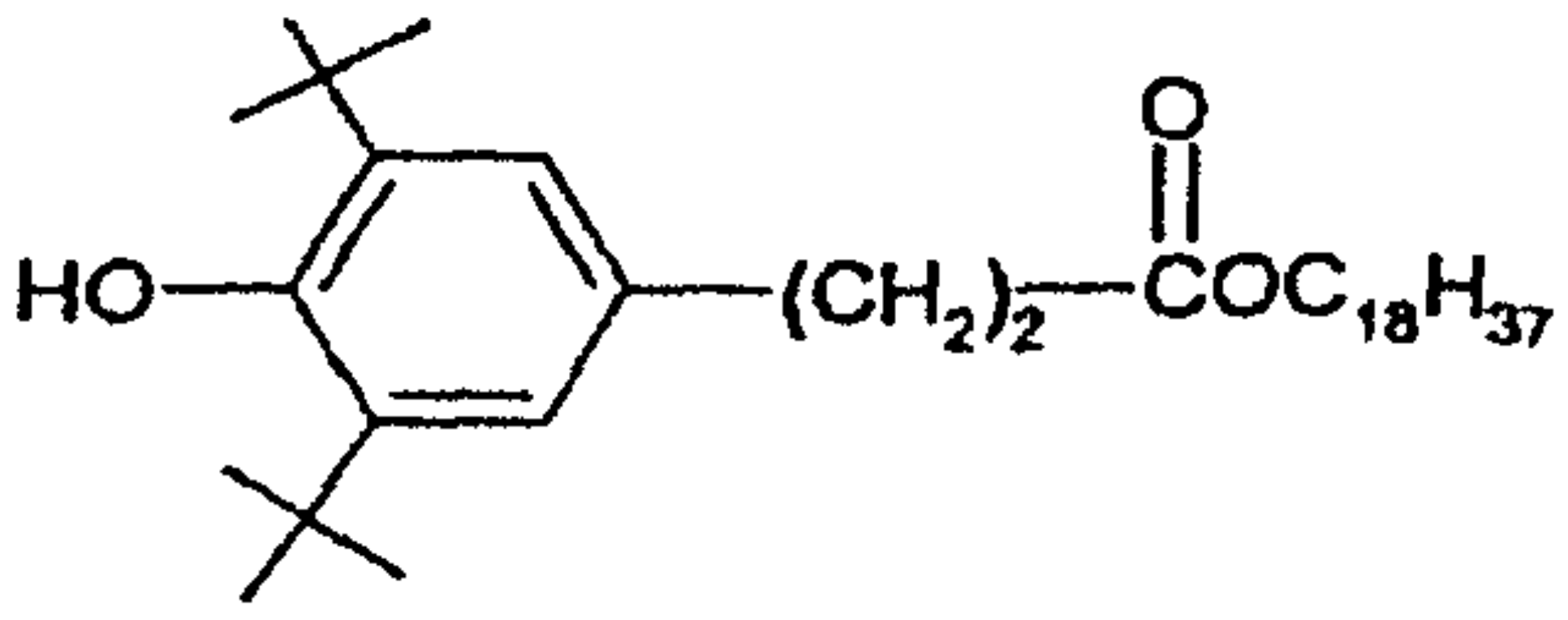
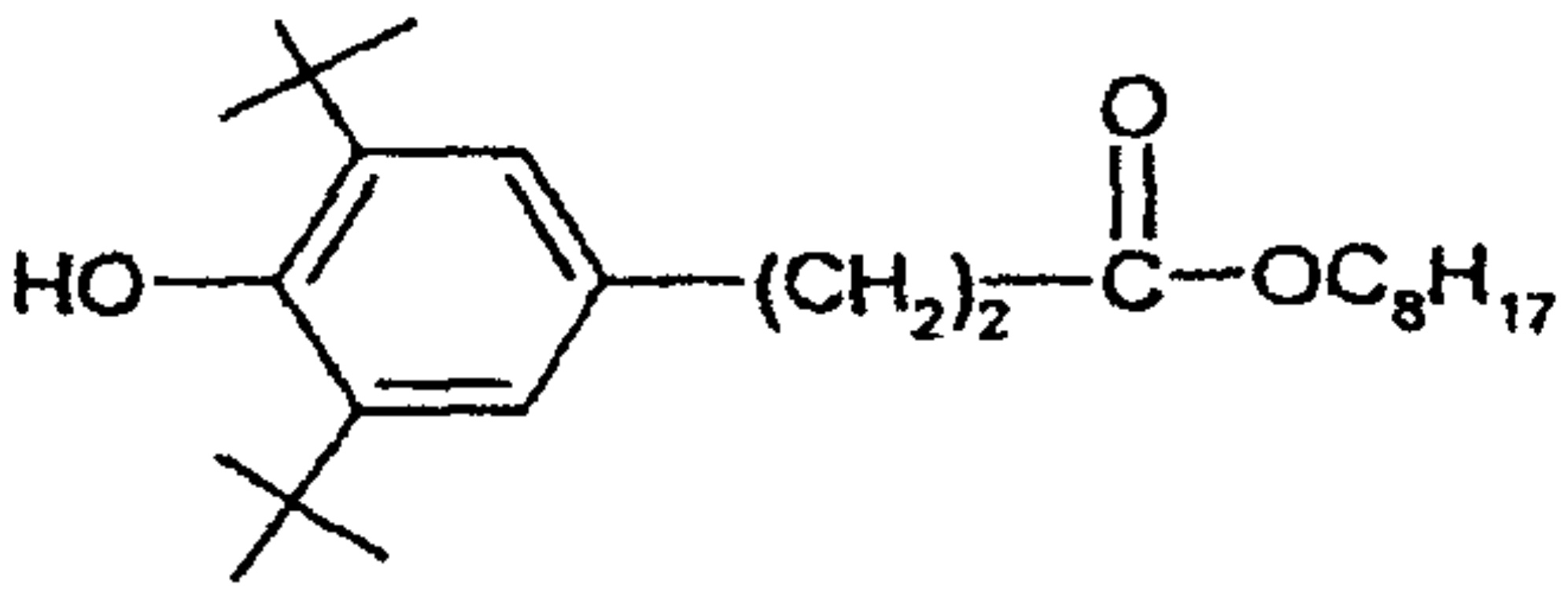
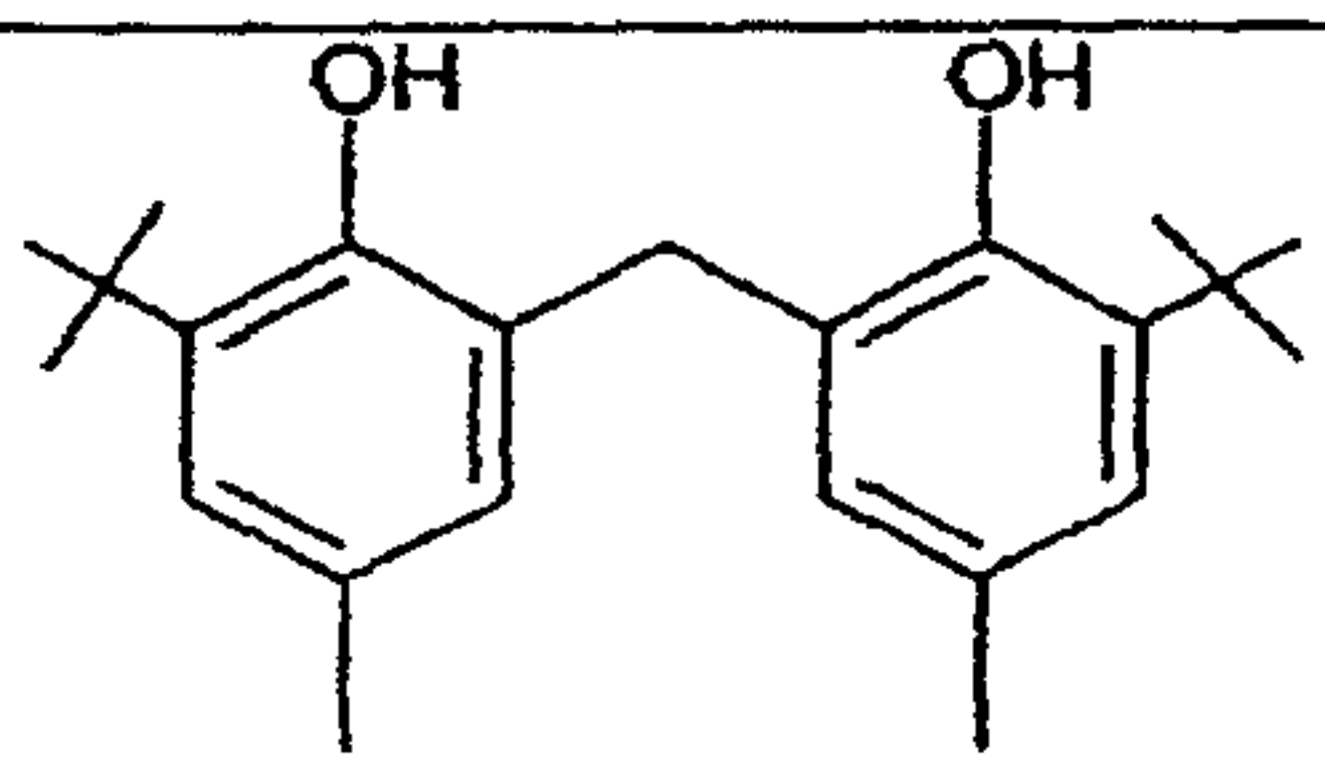
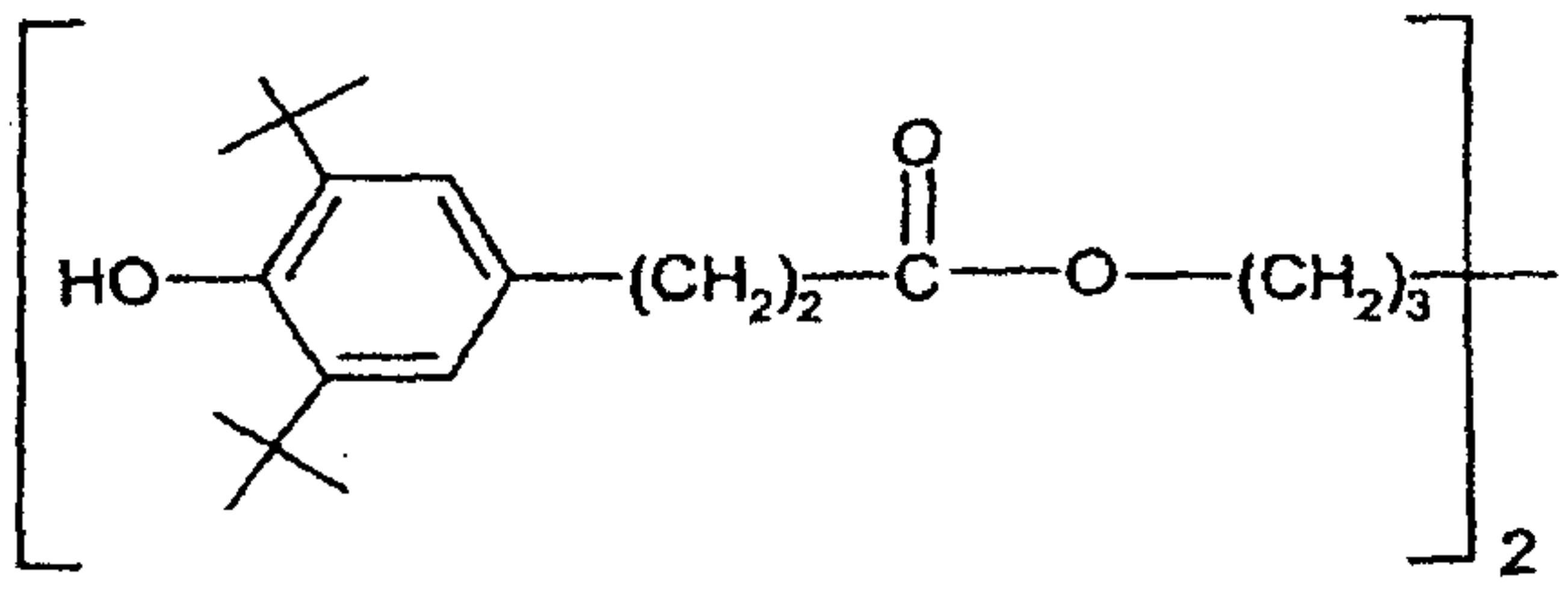
10191-41-0	
128-37-0	
2082-79-3	
12643-61-0	
119-47-1	
35074-77-2	

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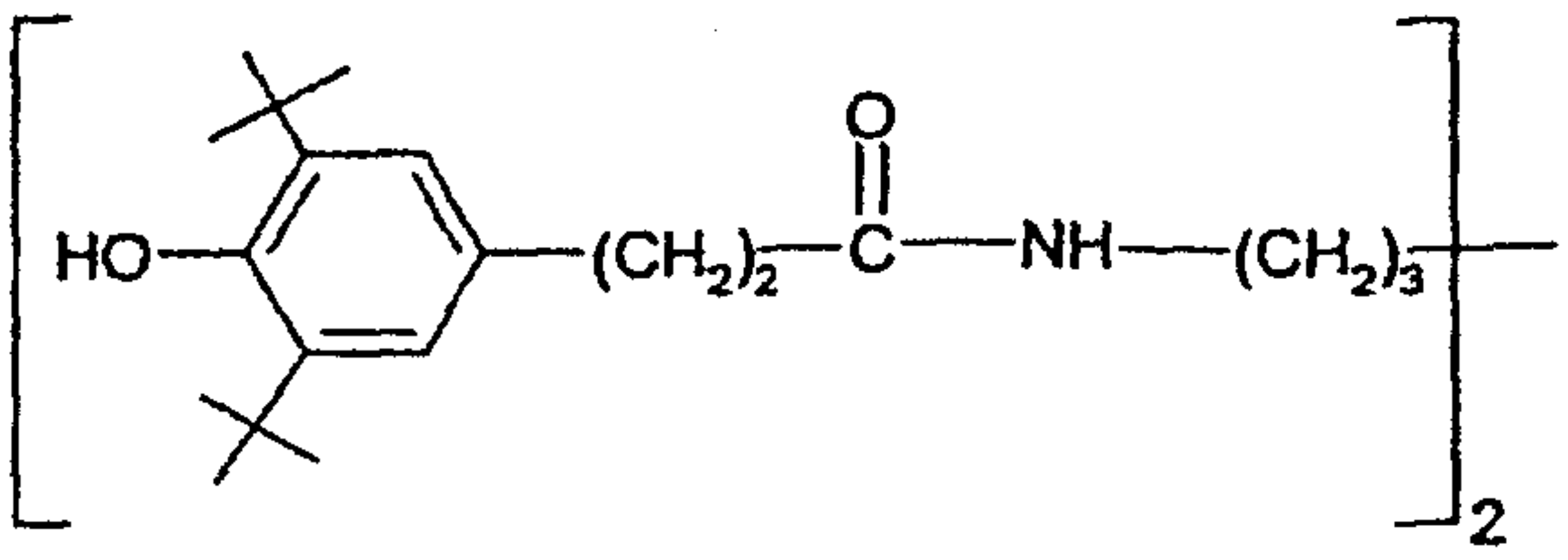
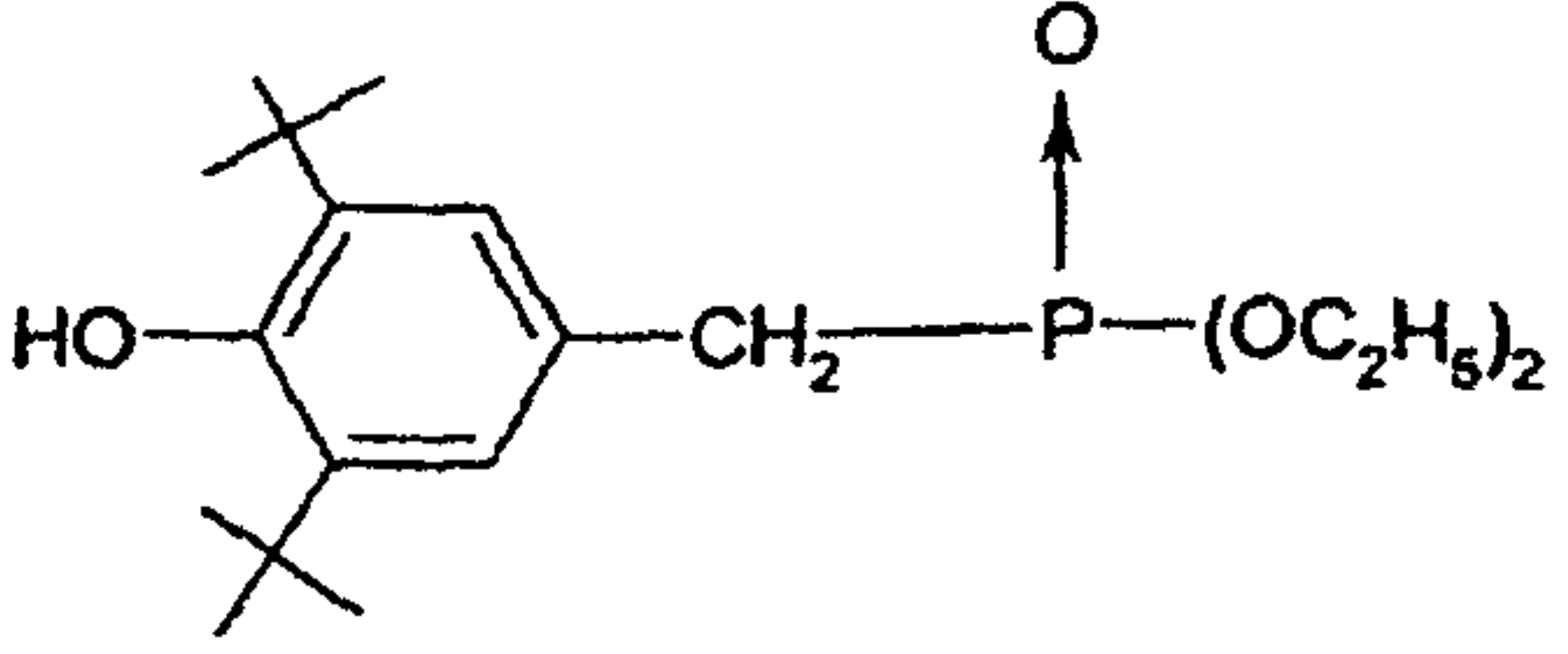
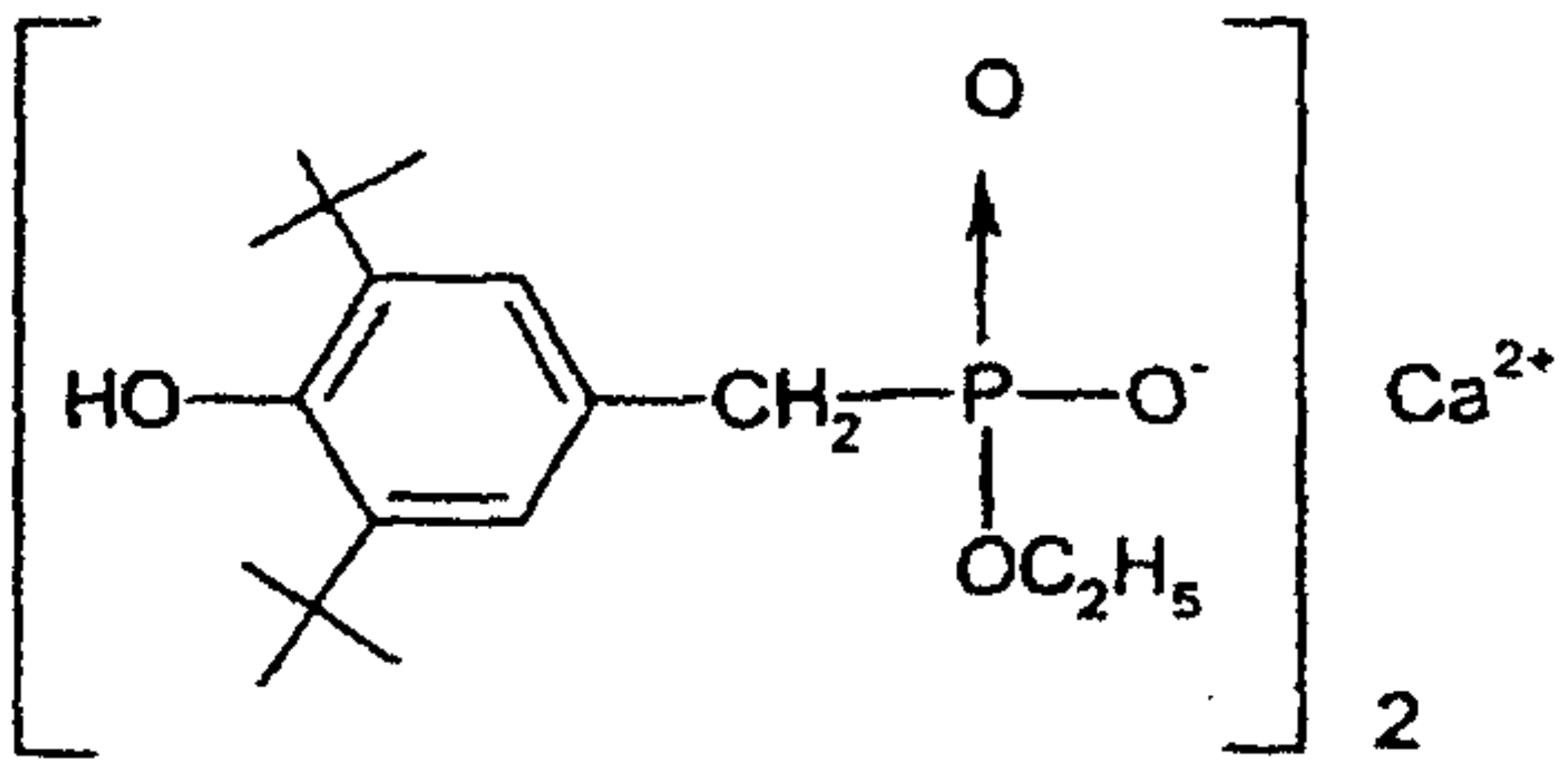
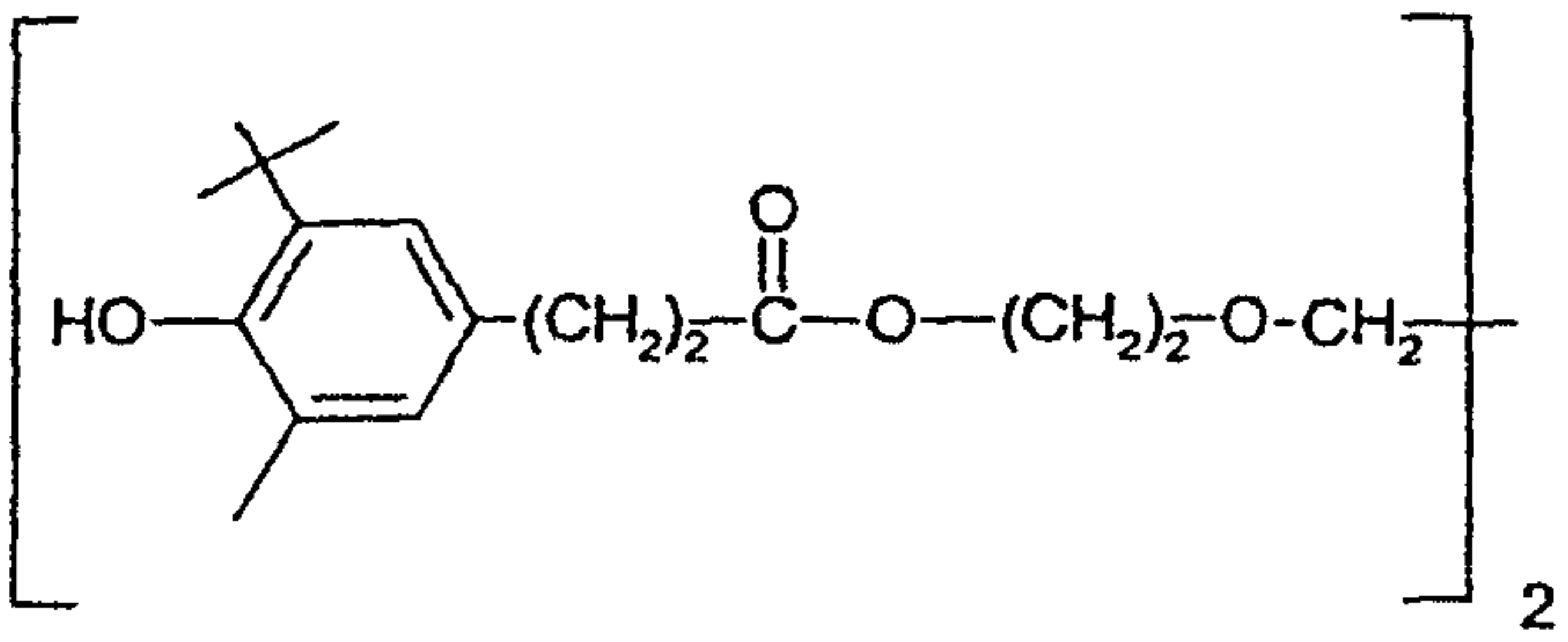
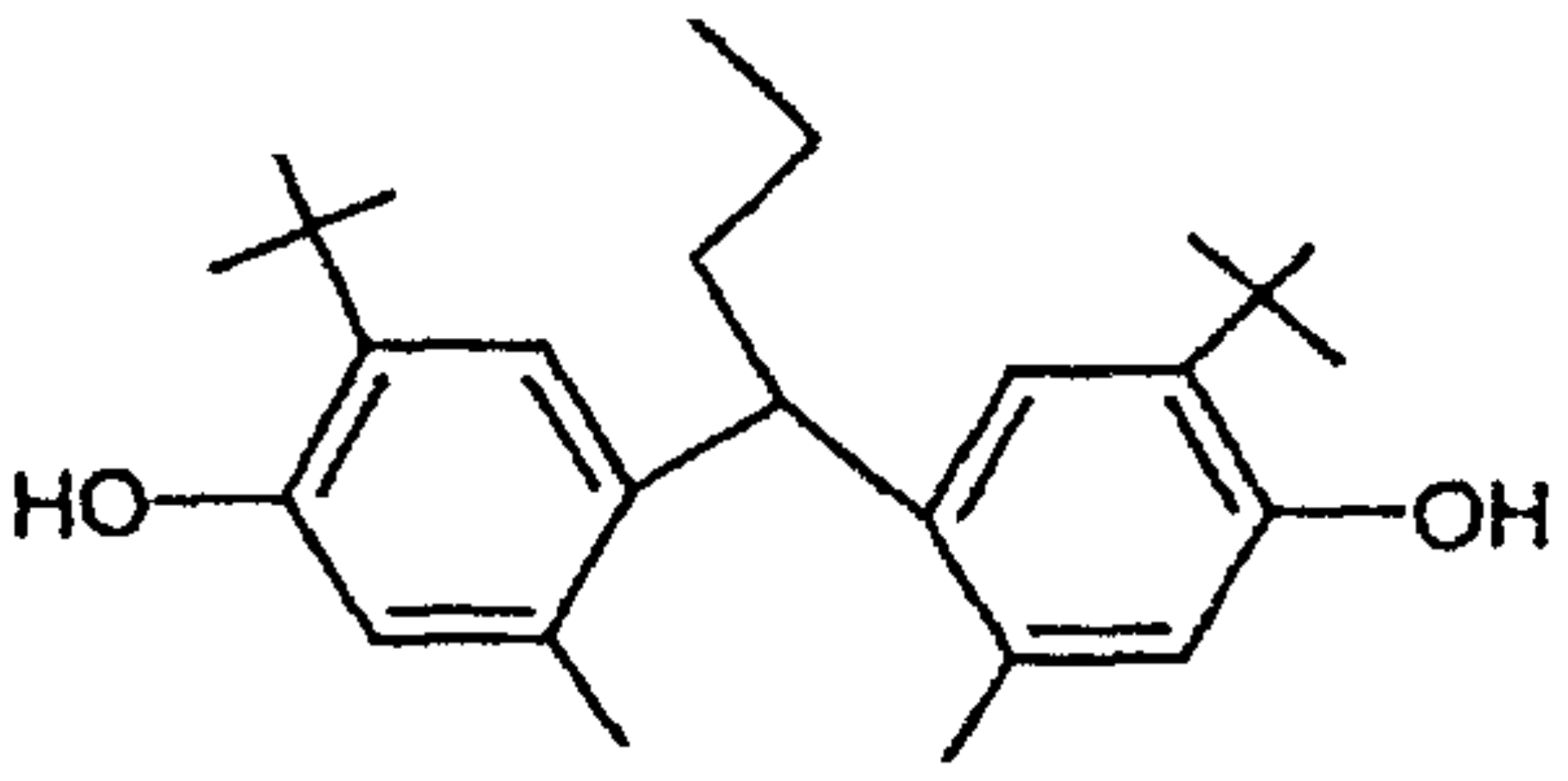
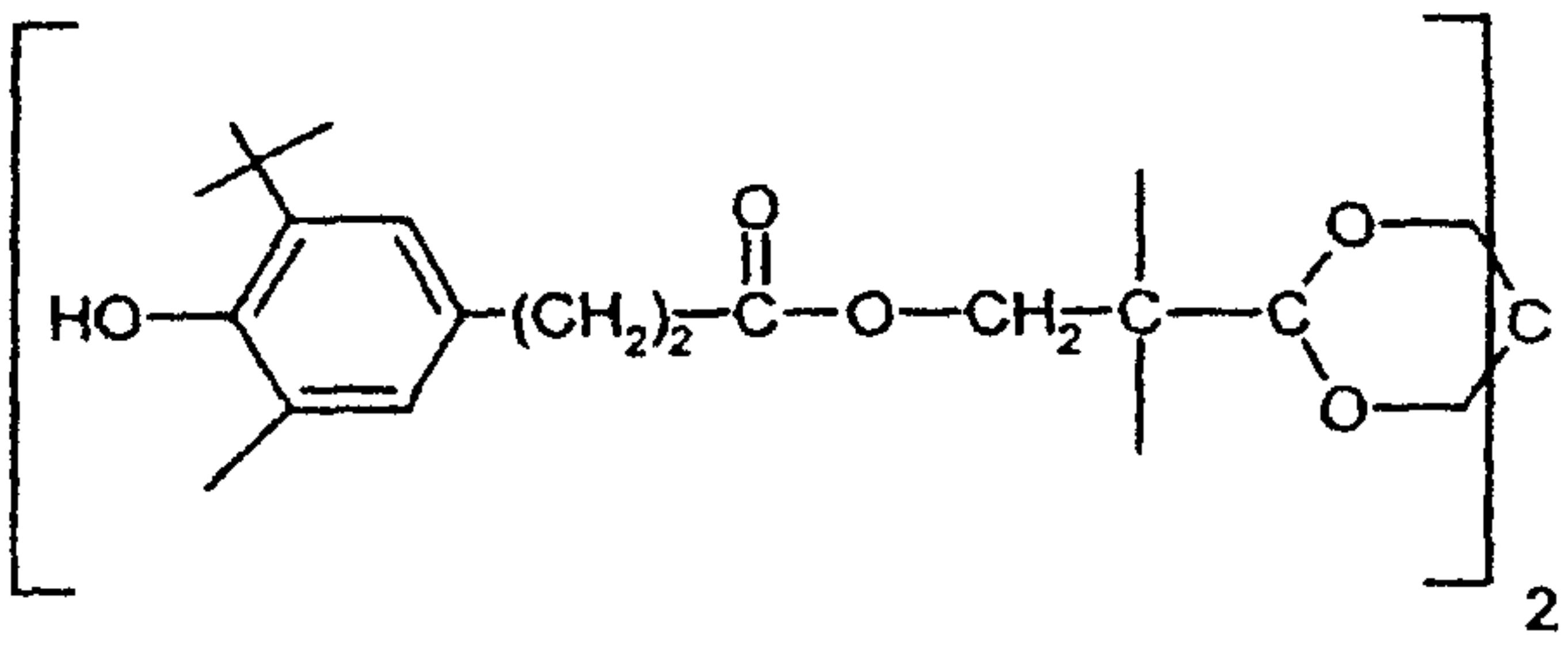
23128-74-7	
976-56-7	
65140-91-2	
36443-68-2	
85-60-9	
90498-90-1	

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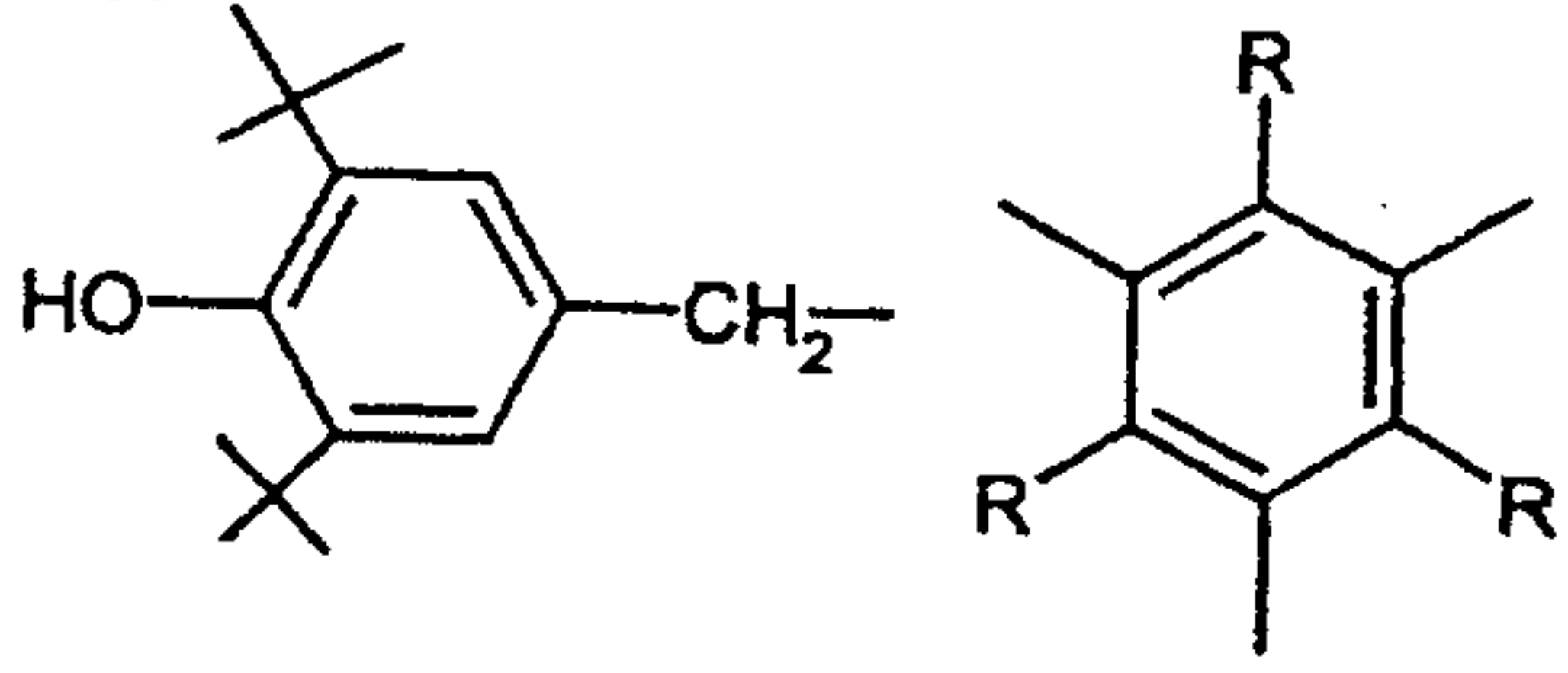
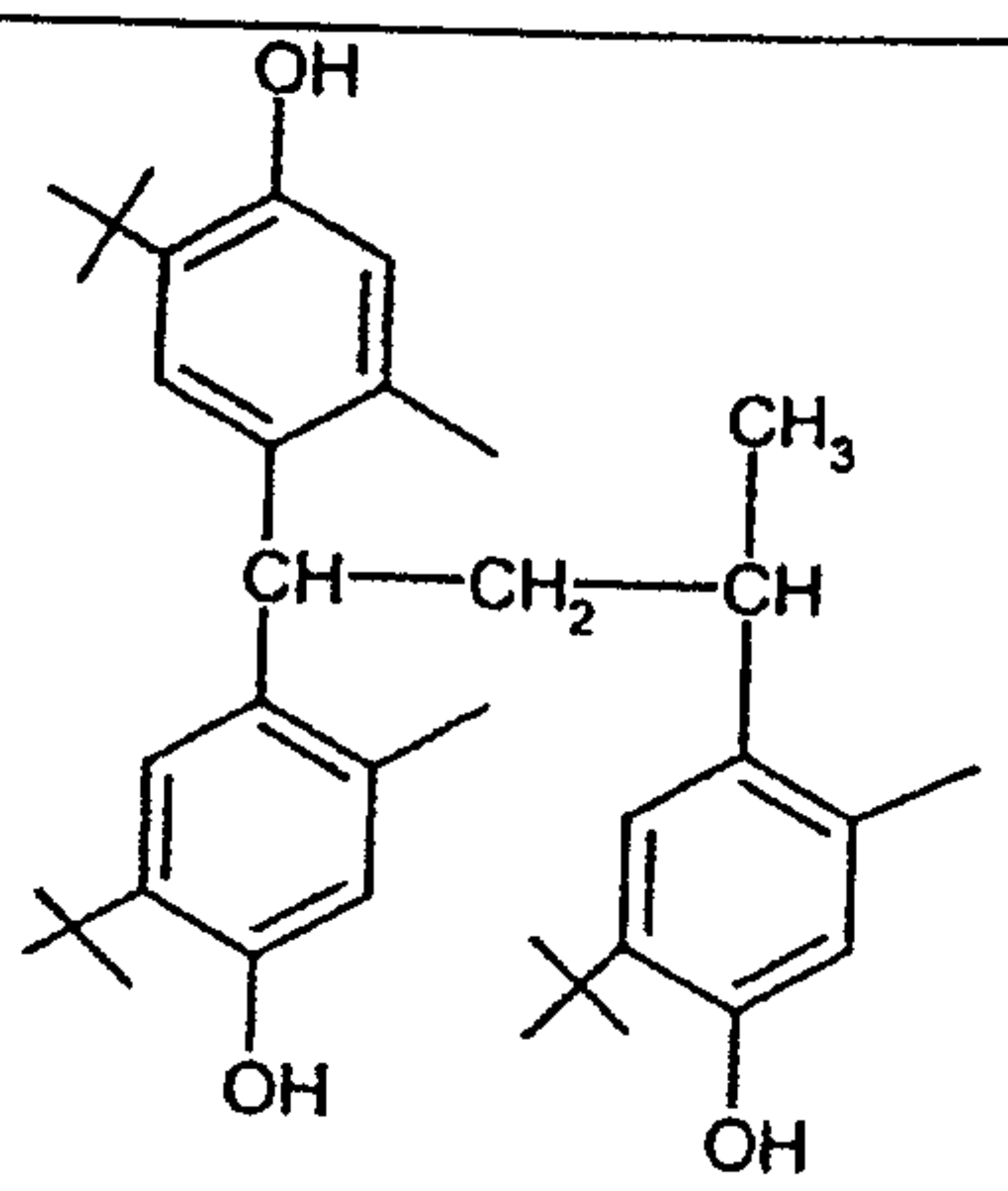
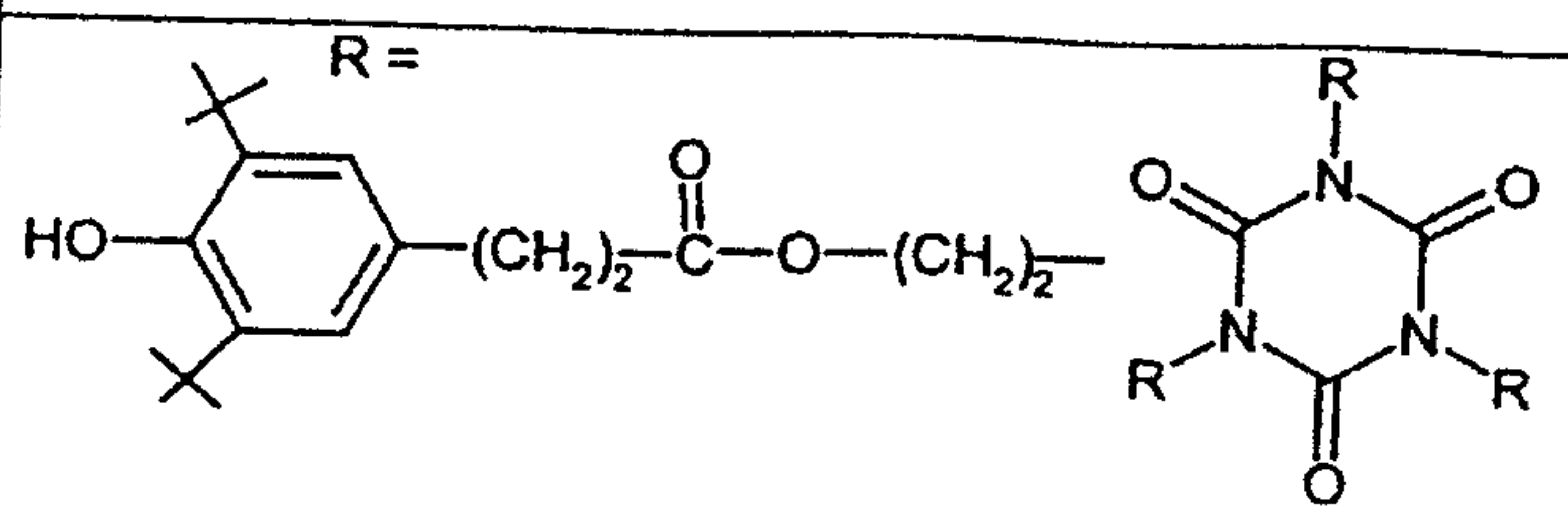
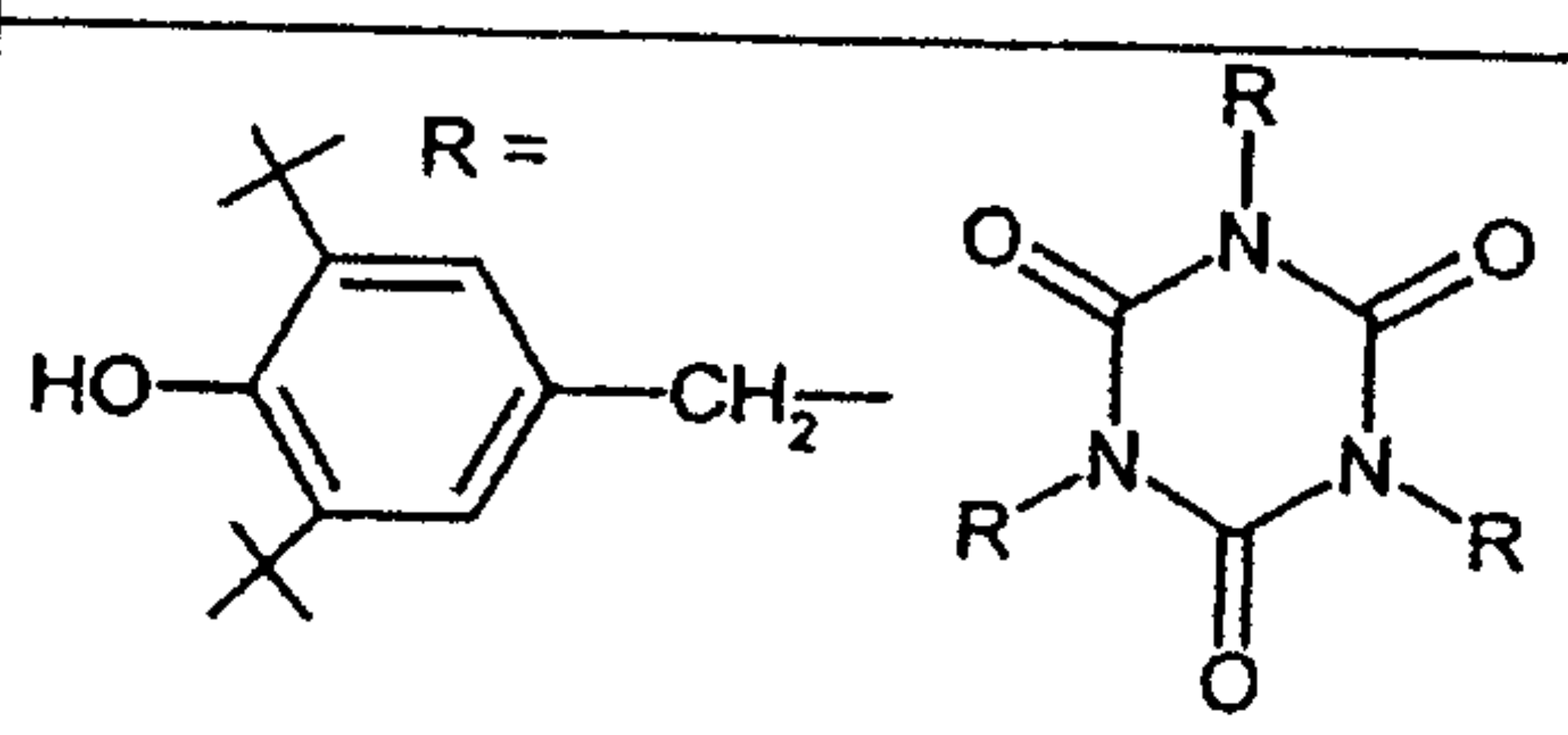
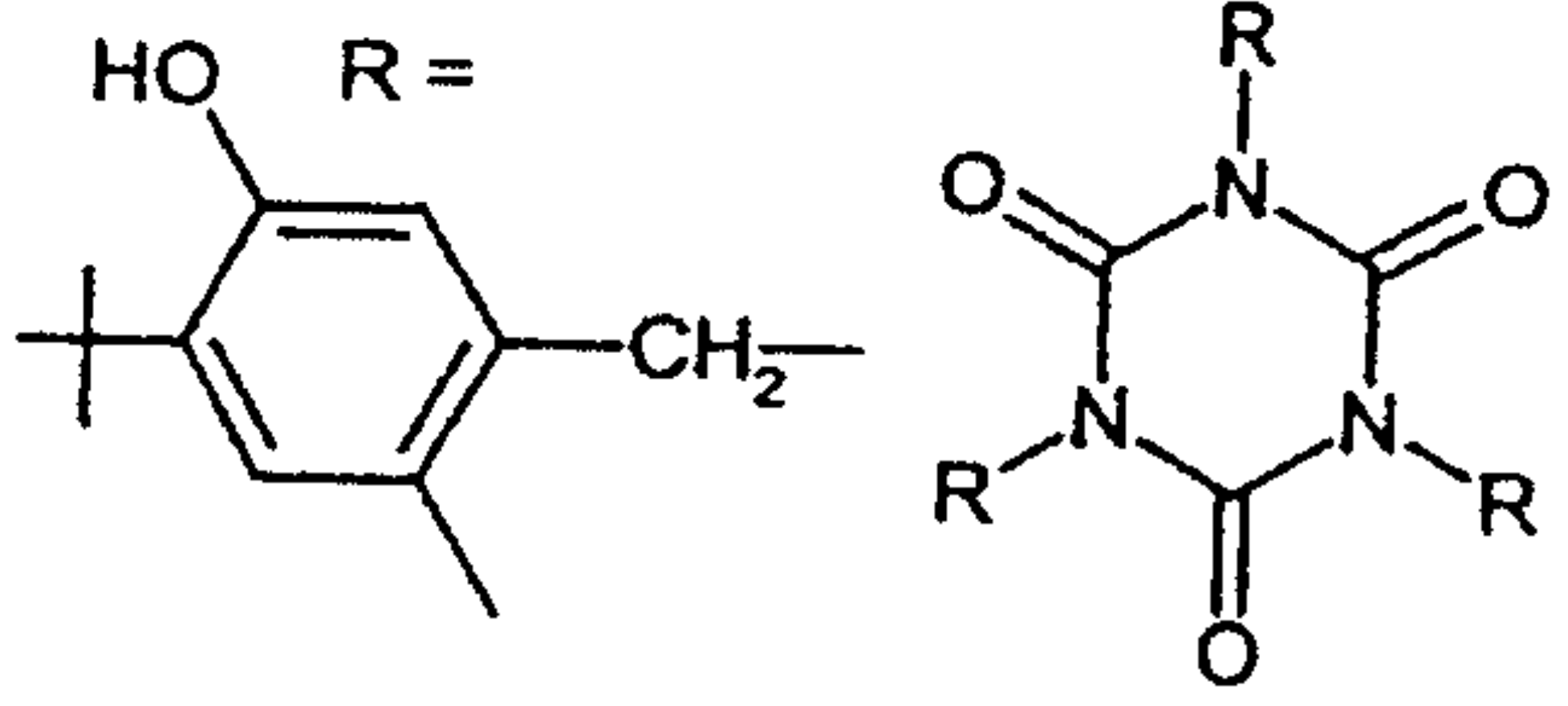
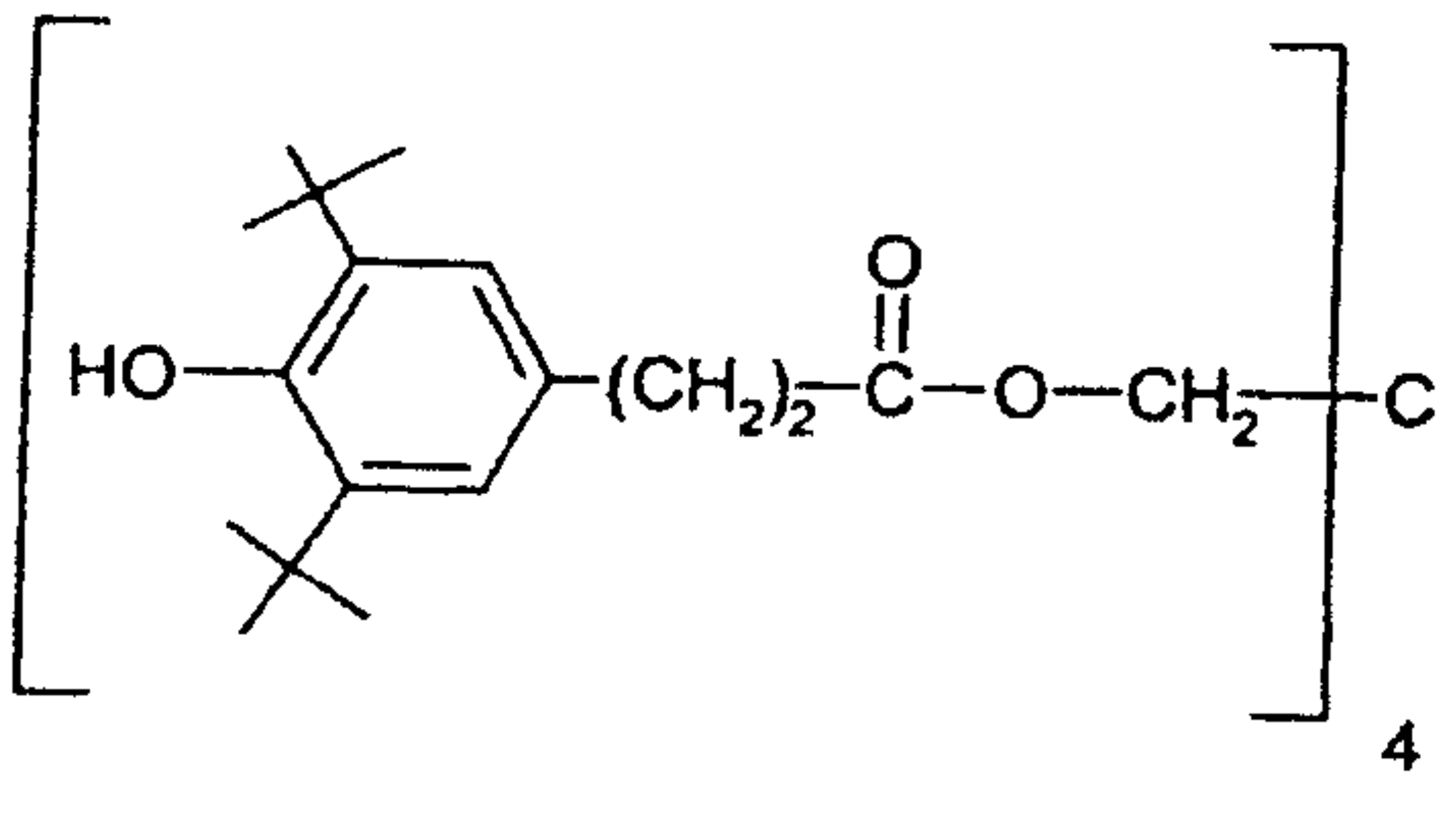
1709-70-2	
1843-03-4	
G34137-09-2	
27676-62-6	
40601-76-1	
6683-19-8	

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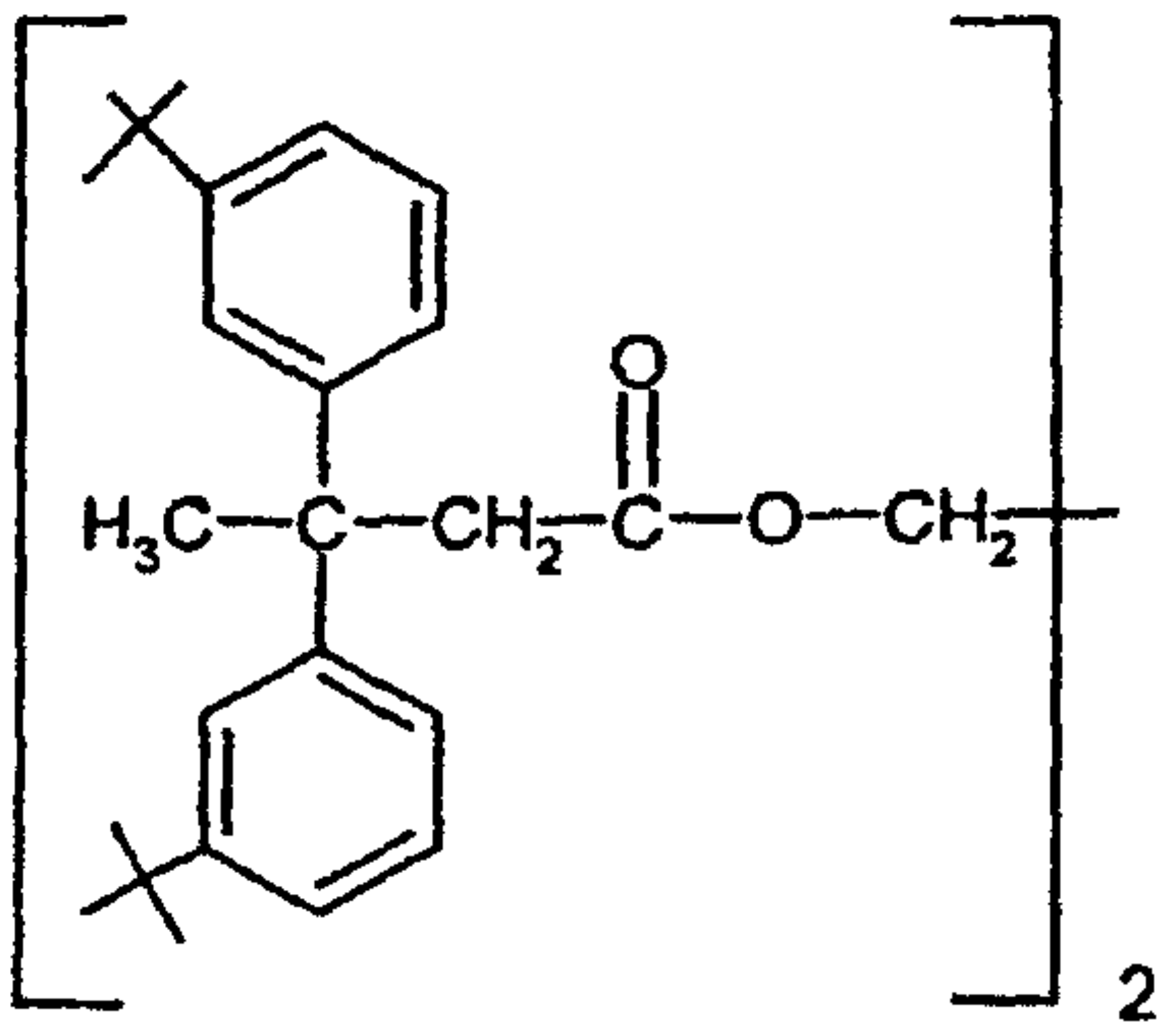
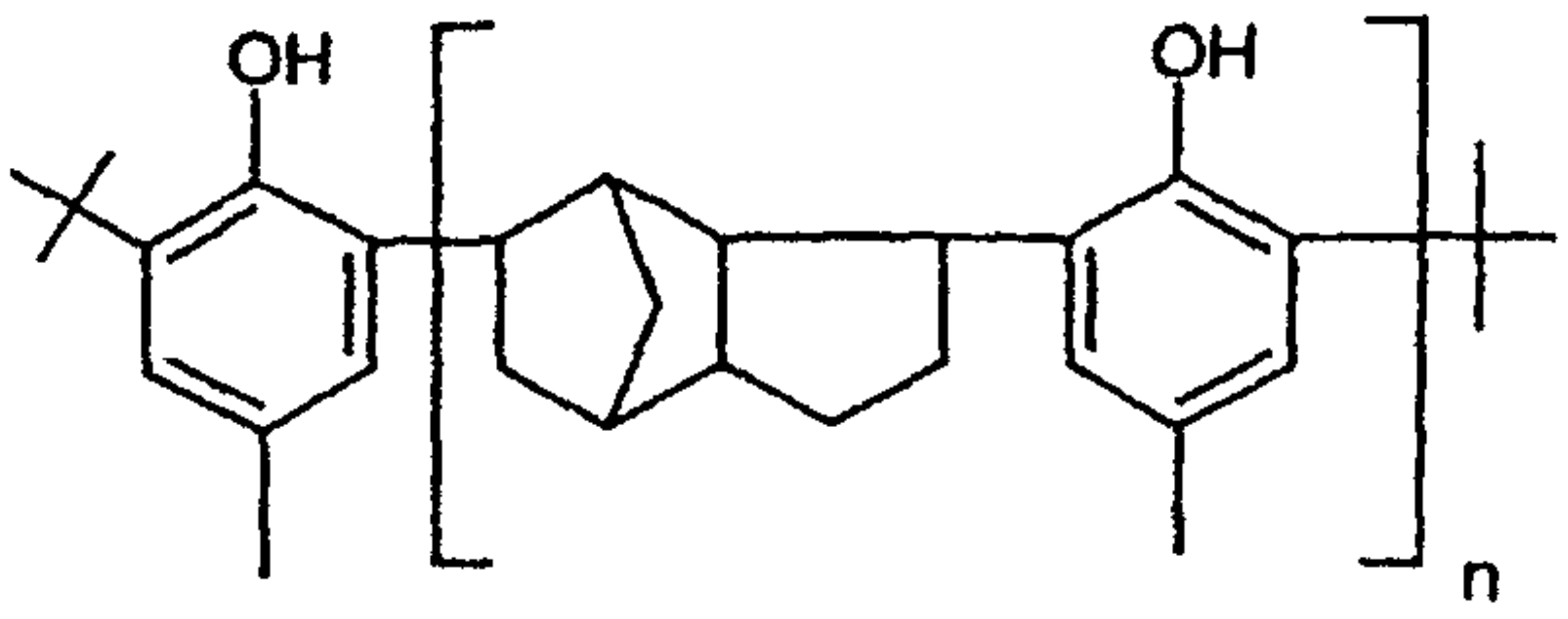
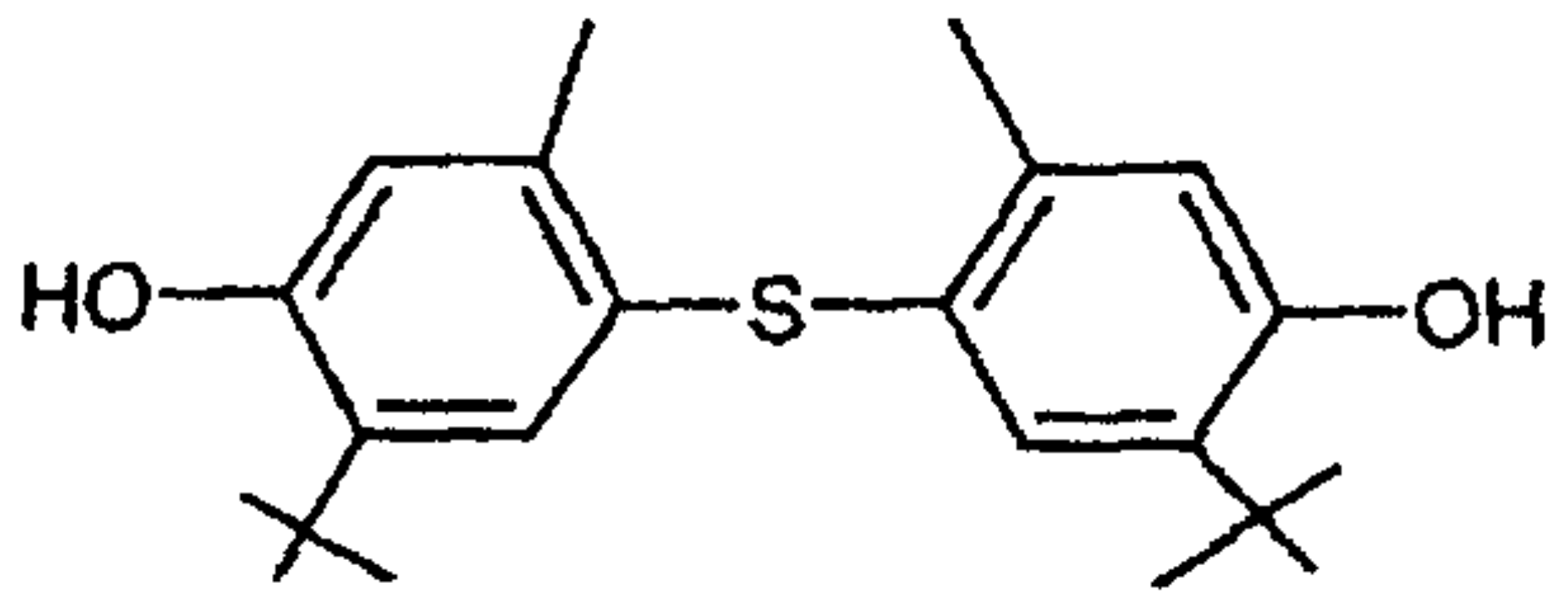
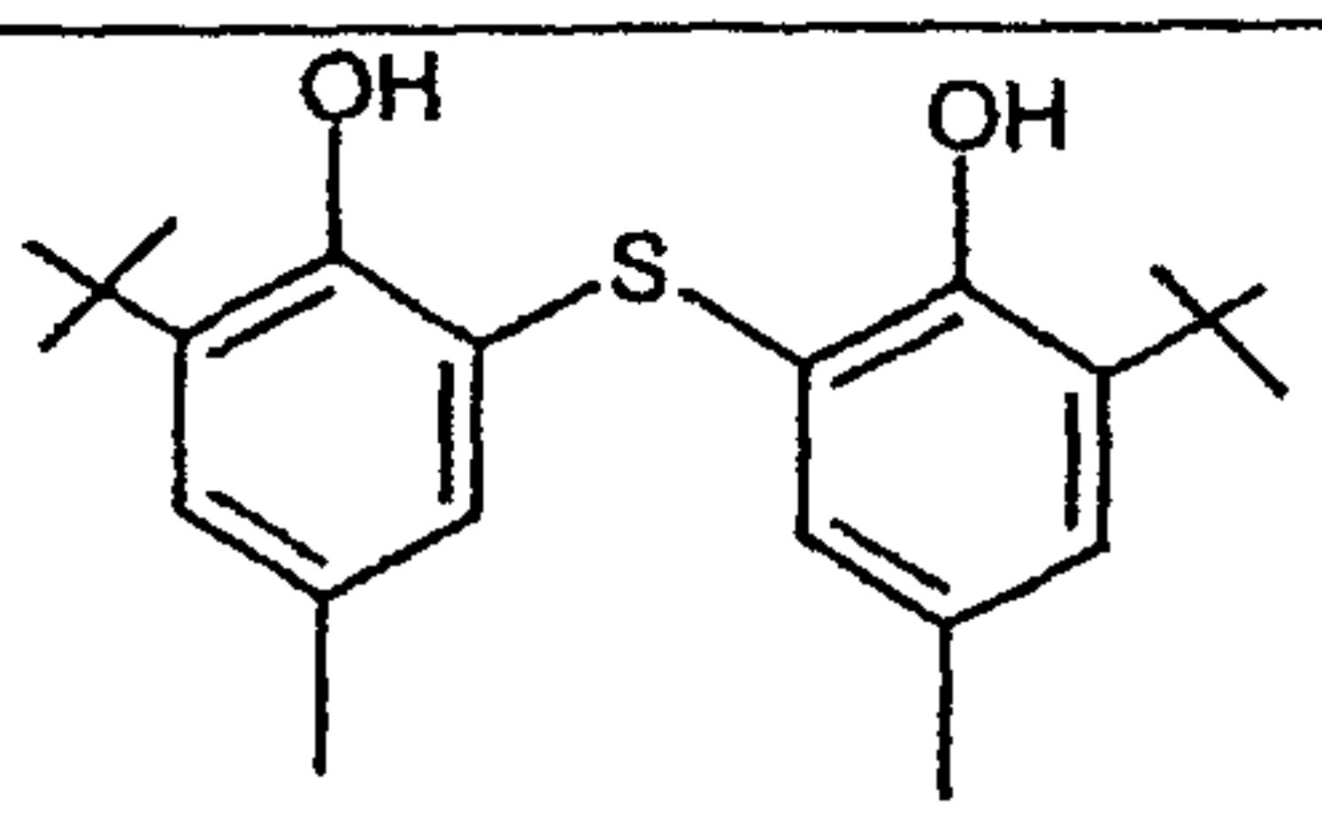
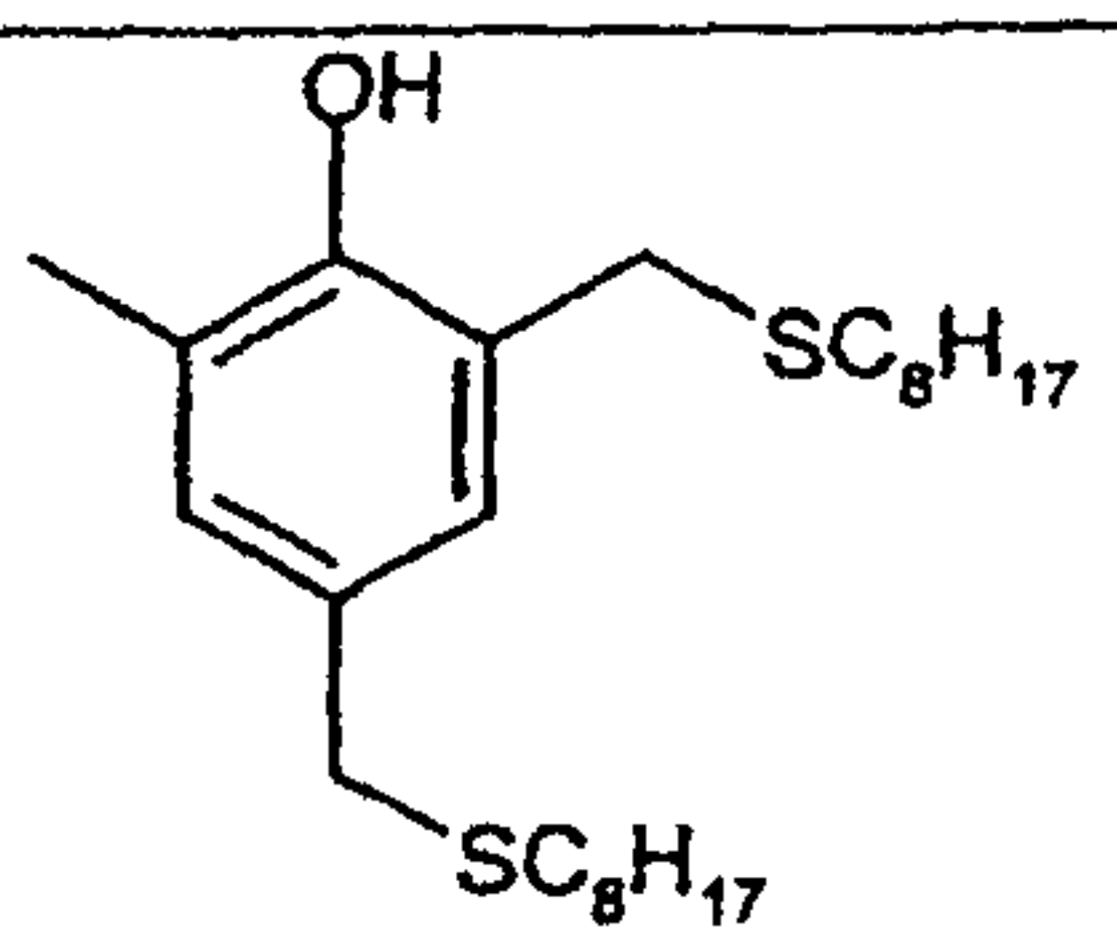
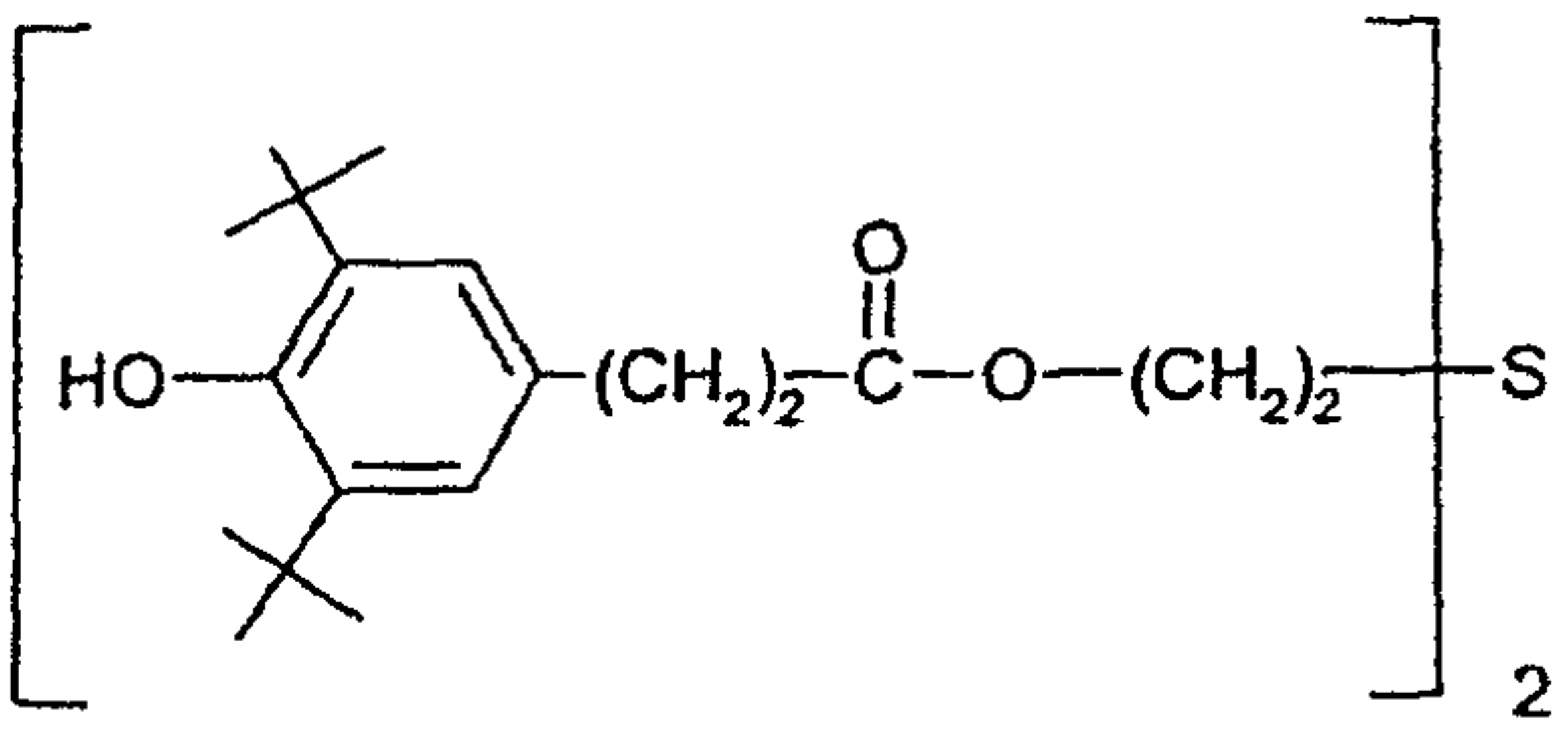
32509-66-3	
31851-03-3	
96-69-5	
90-66-4	
110553-27-0	
41484-35-9	

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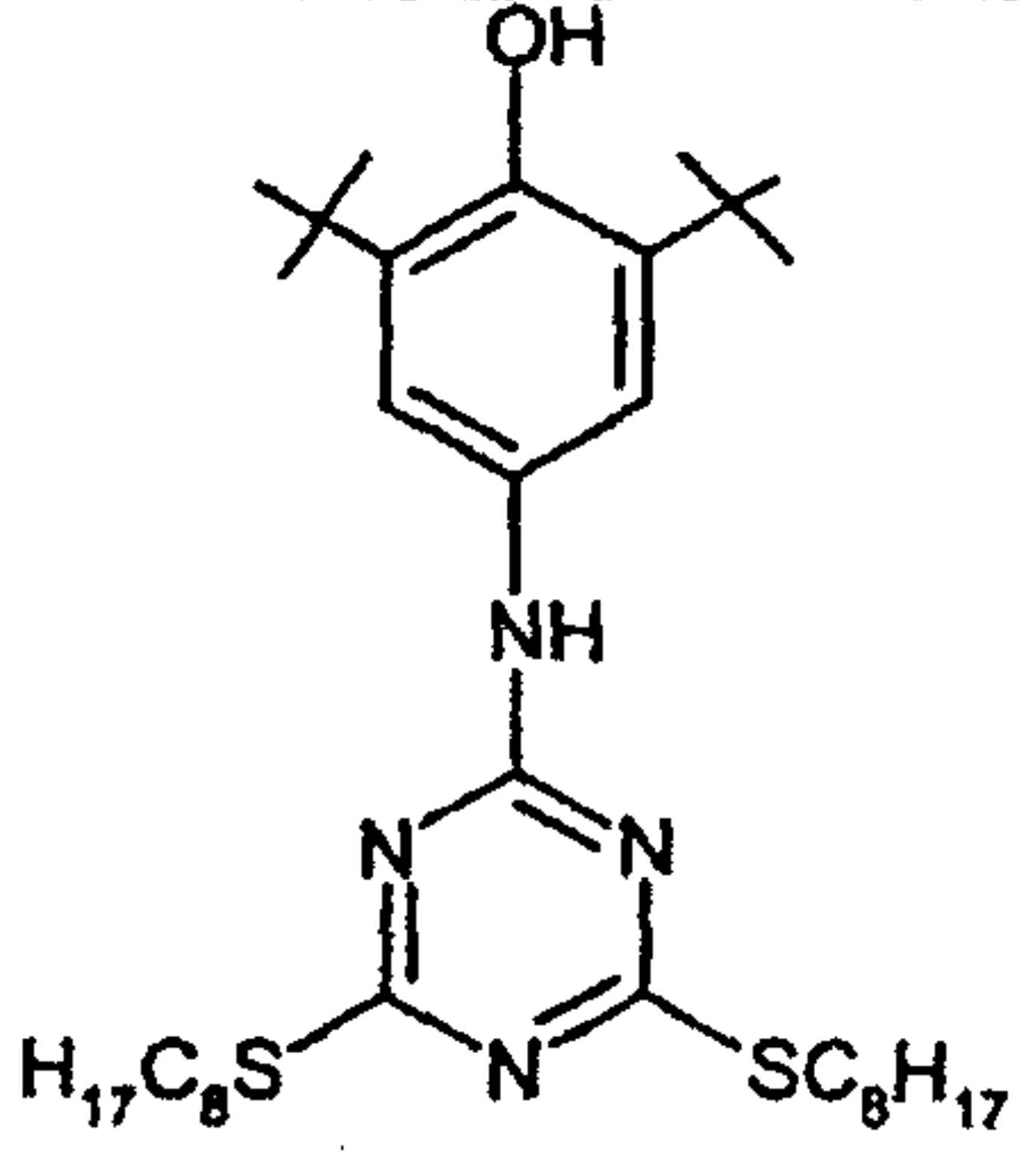
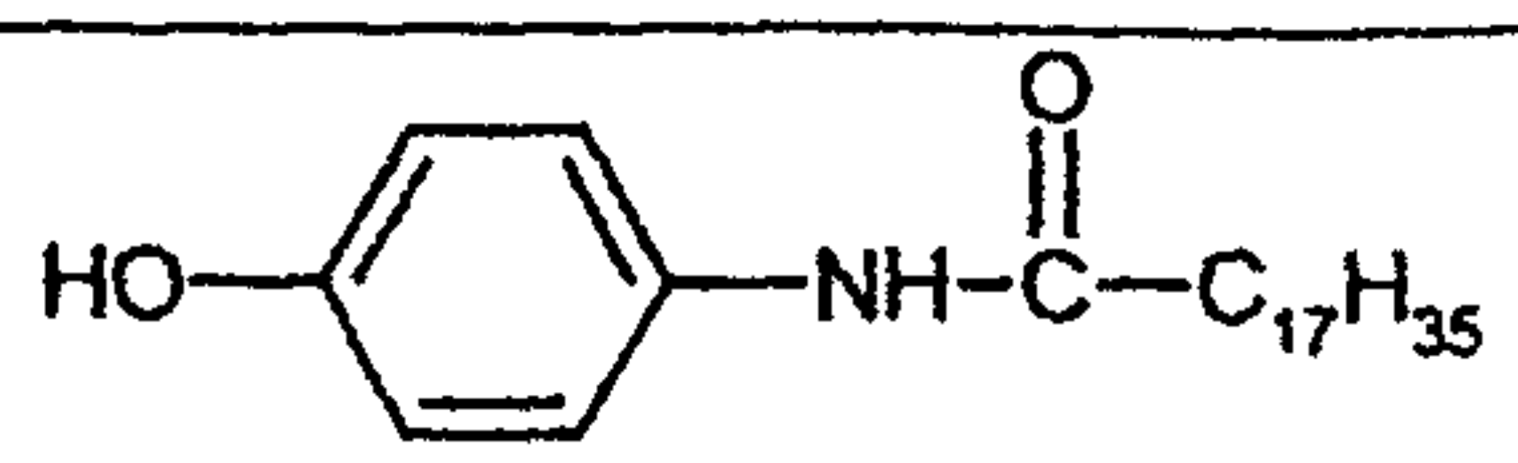
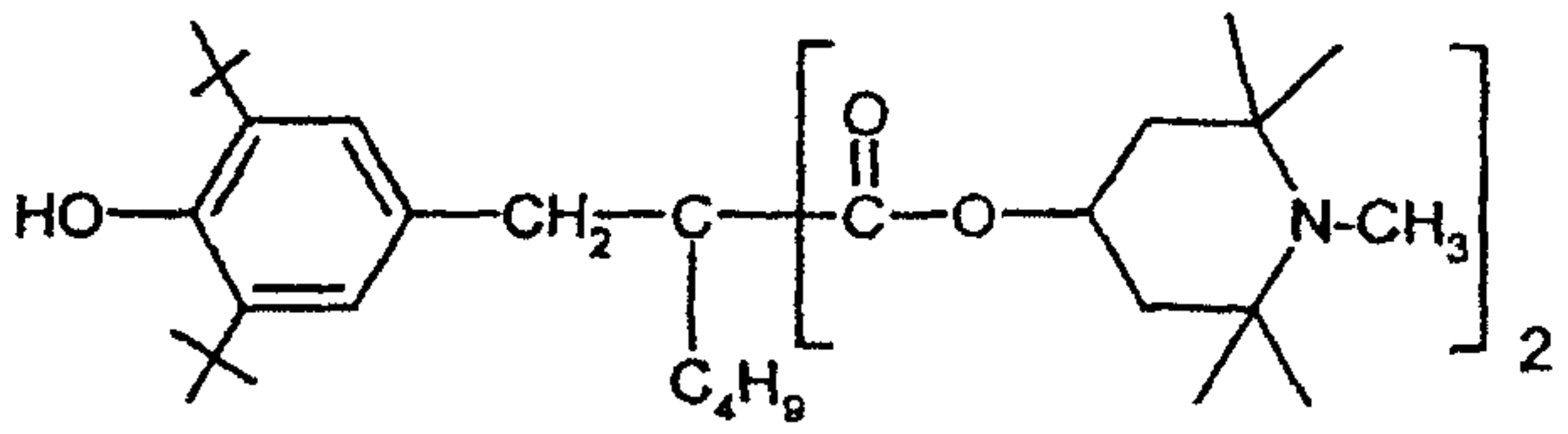
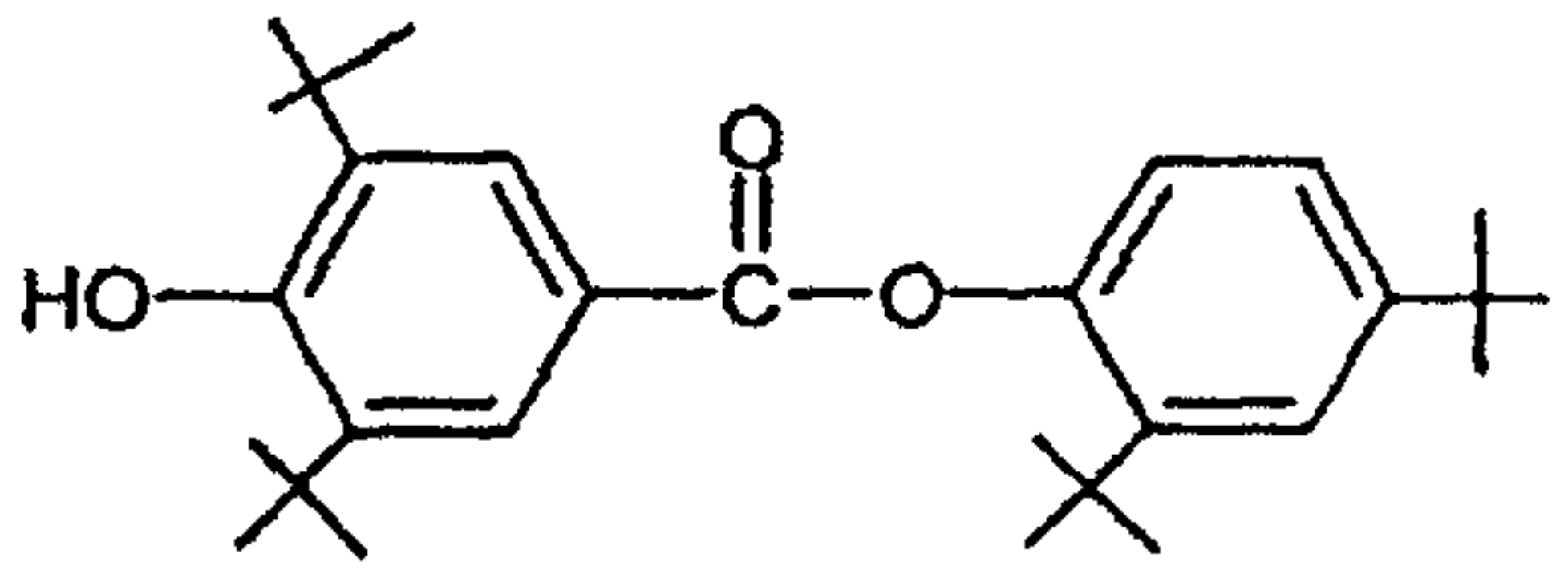
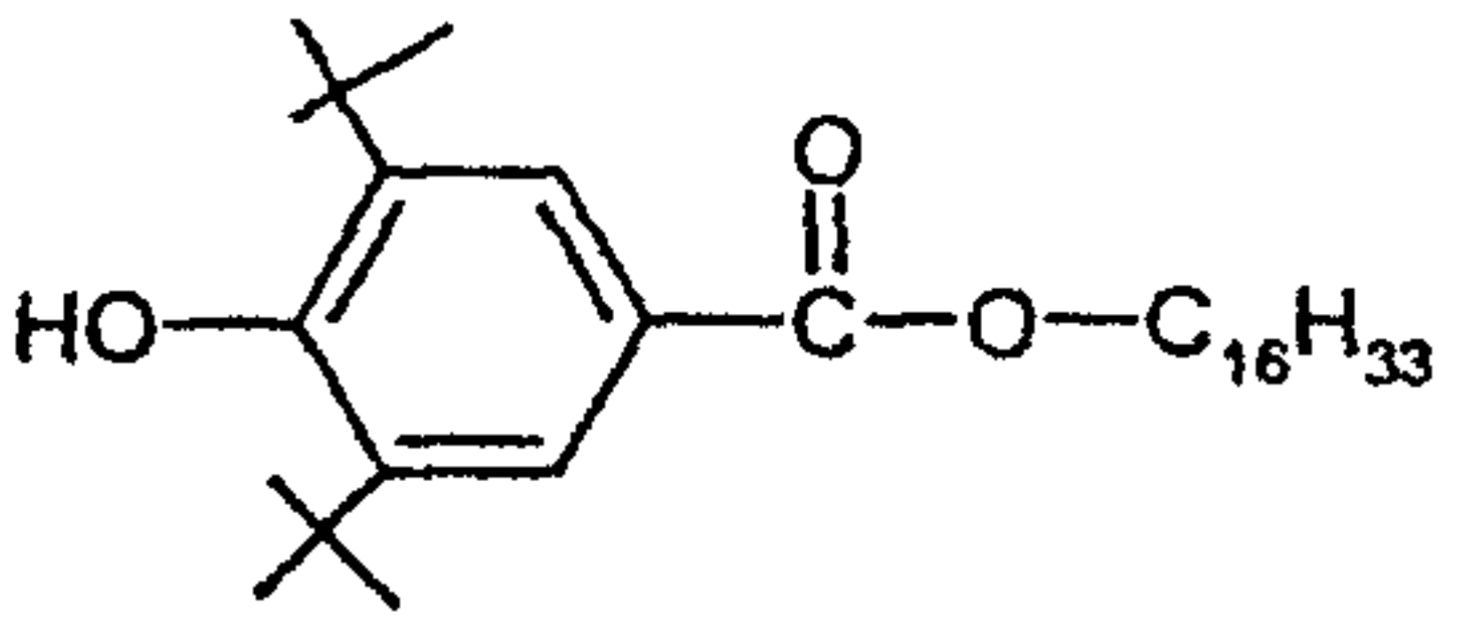
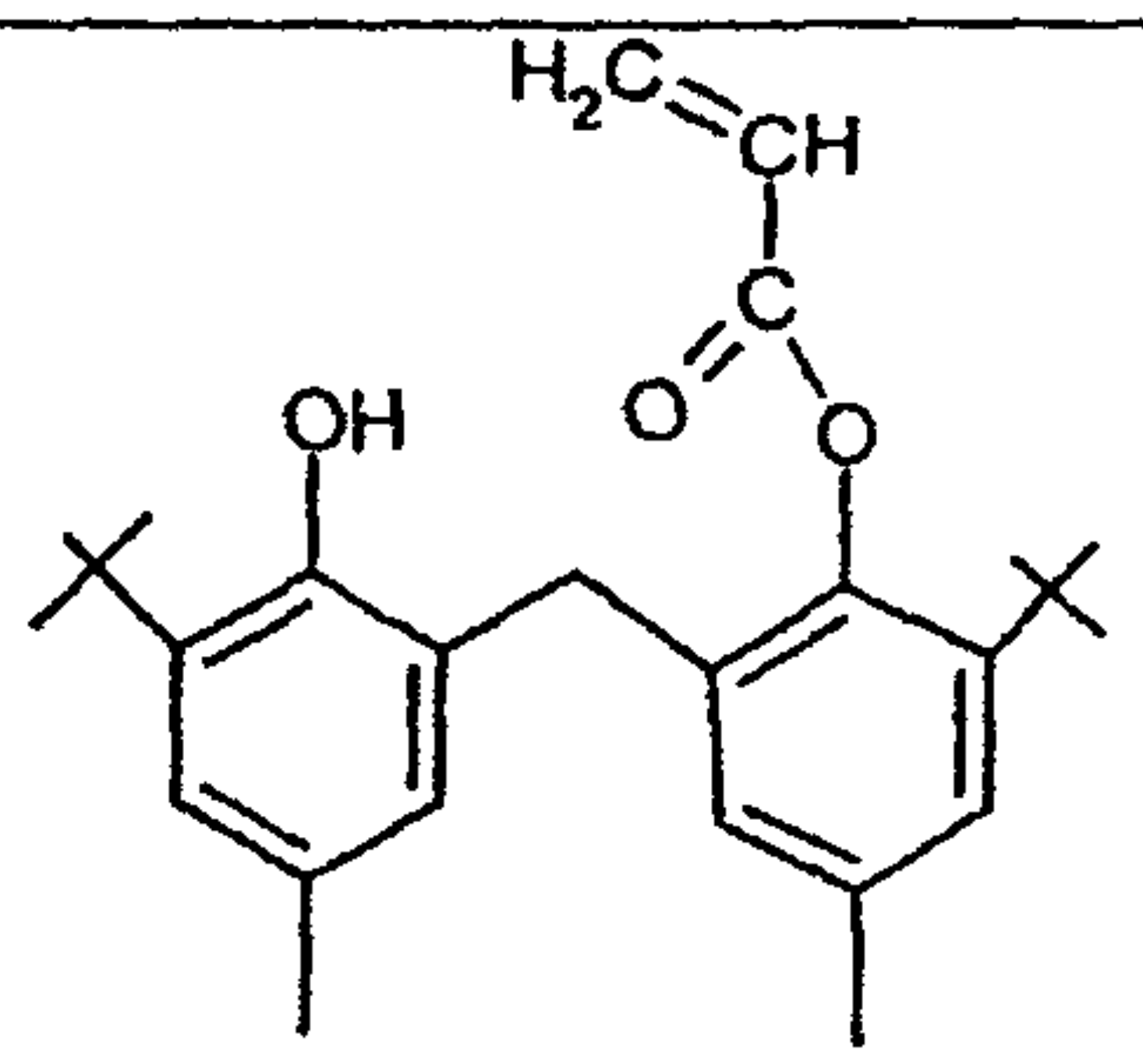
991-84-4	
103-99-1	
63843-89-0	
4221-80-1	
67845-93-6	
61167-58-6	

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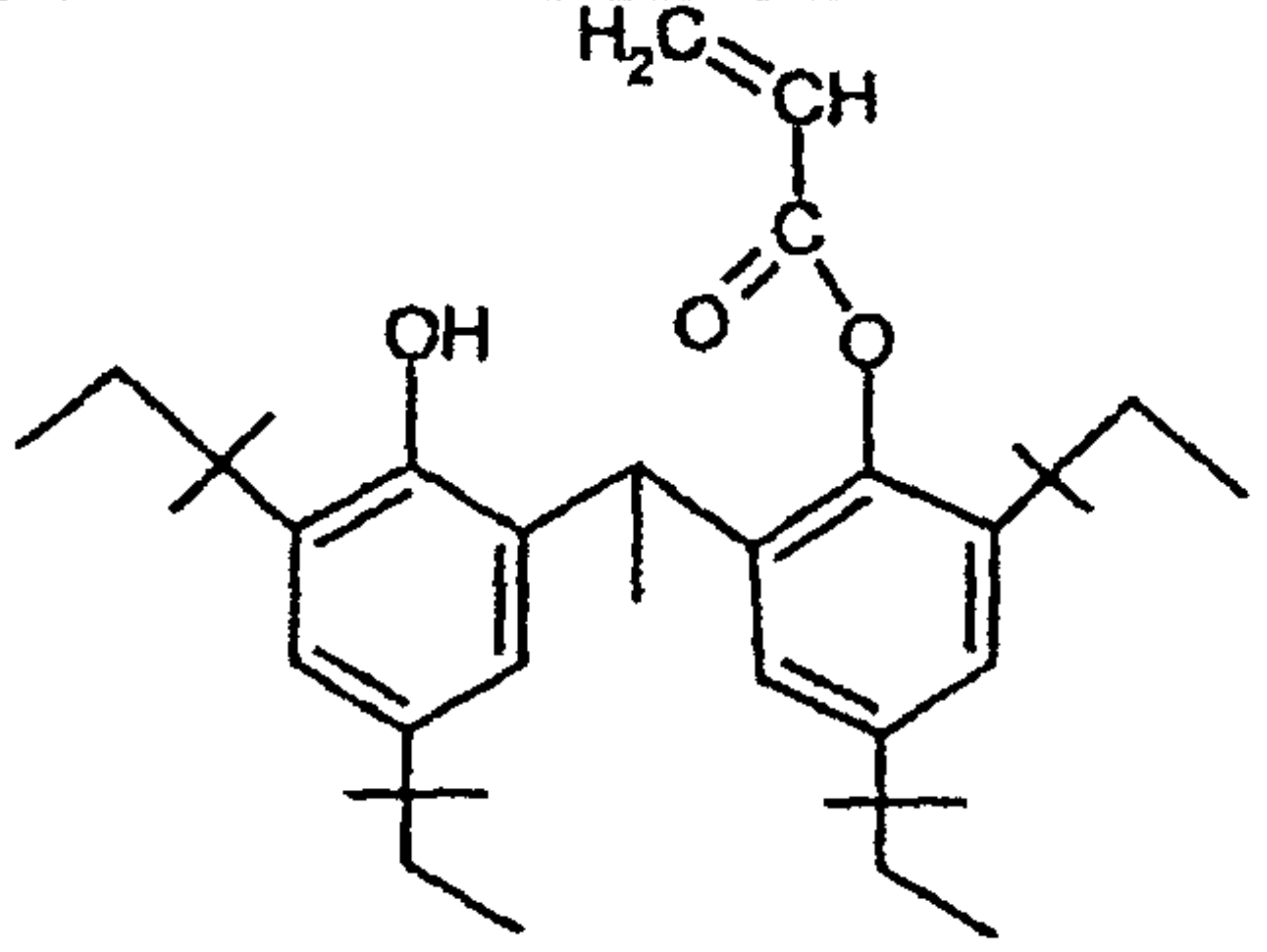
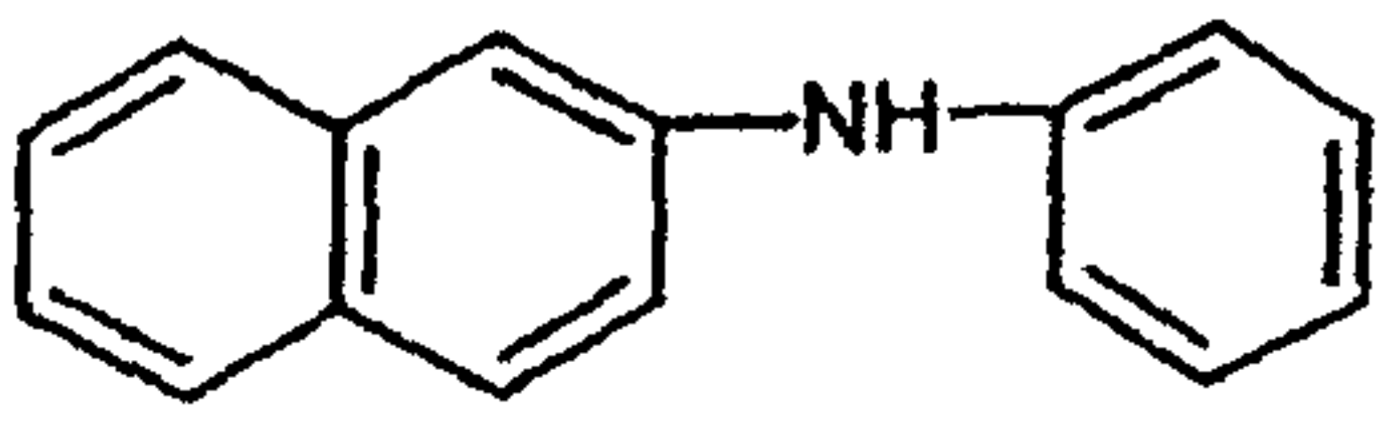
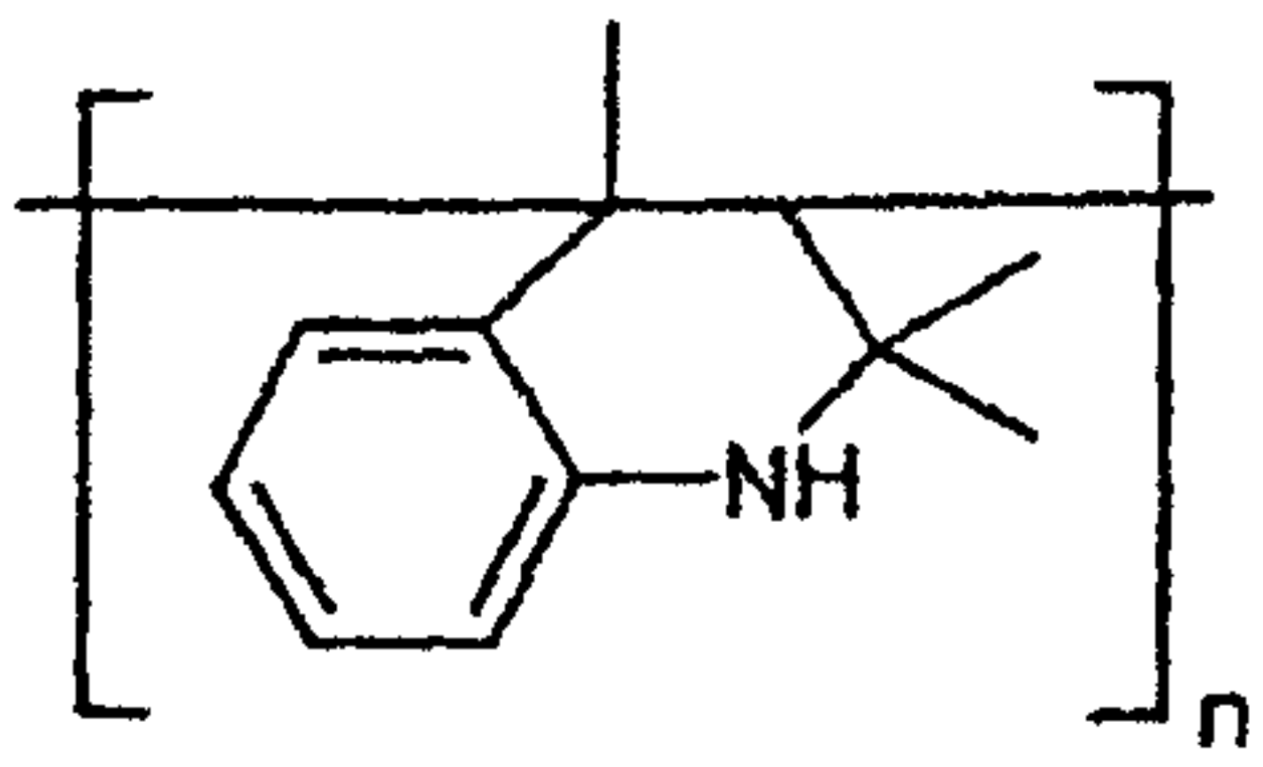
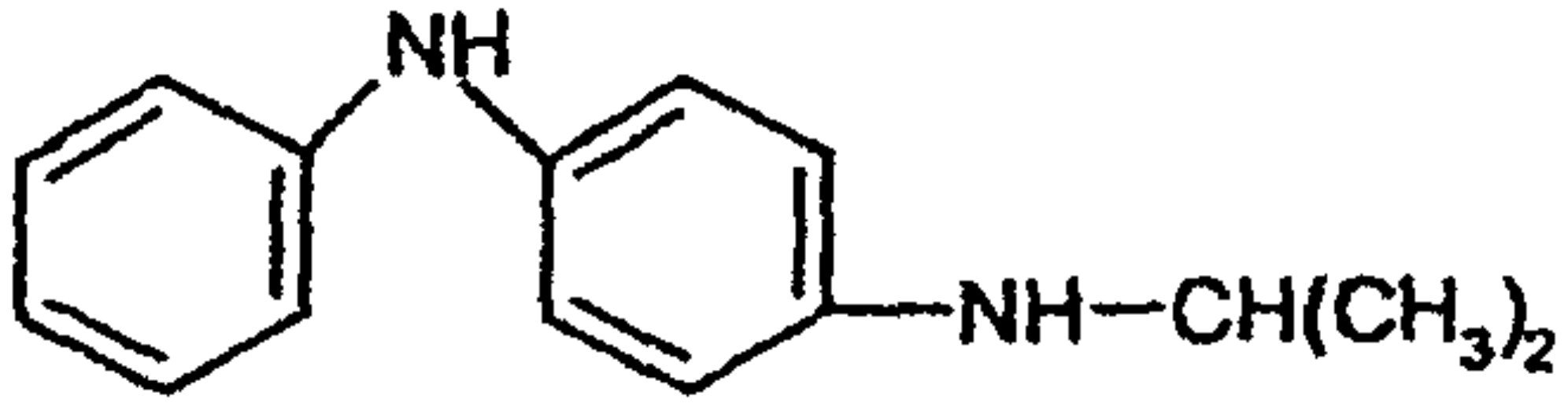
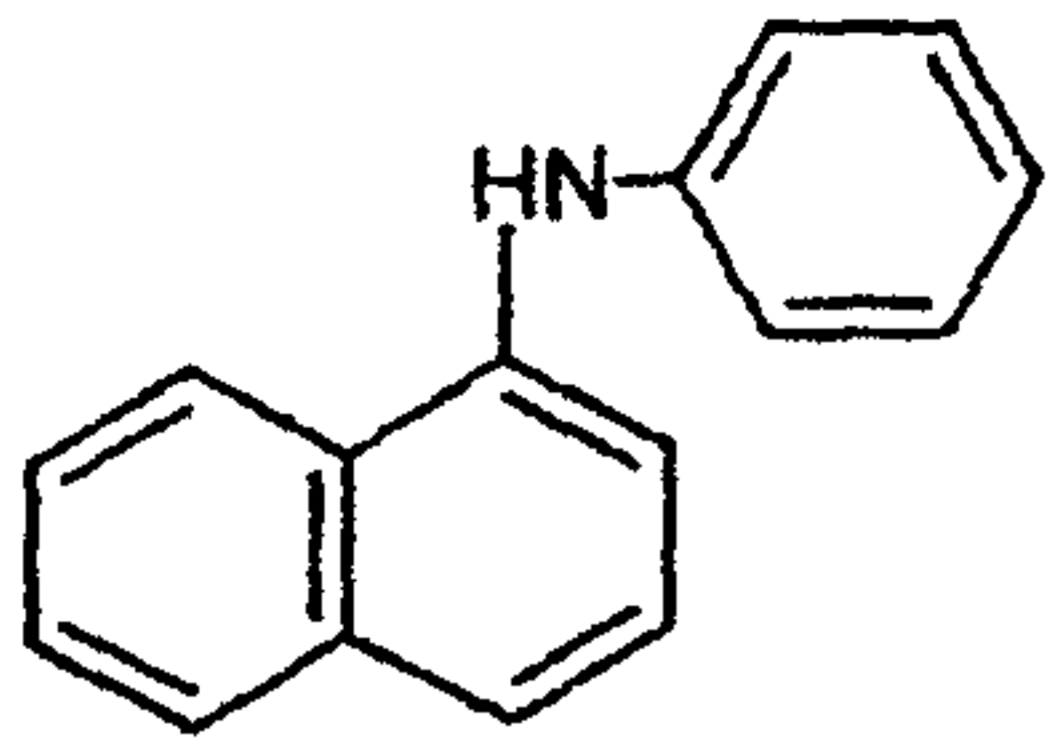
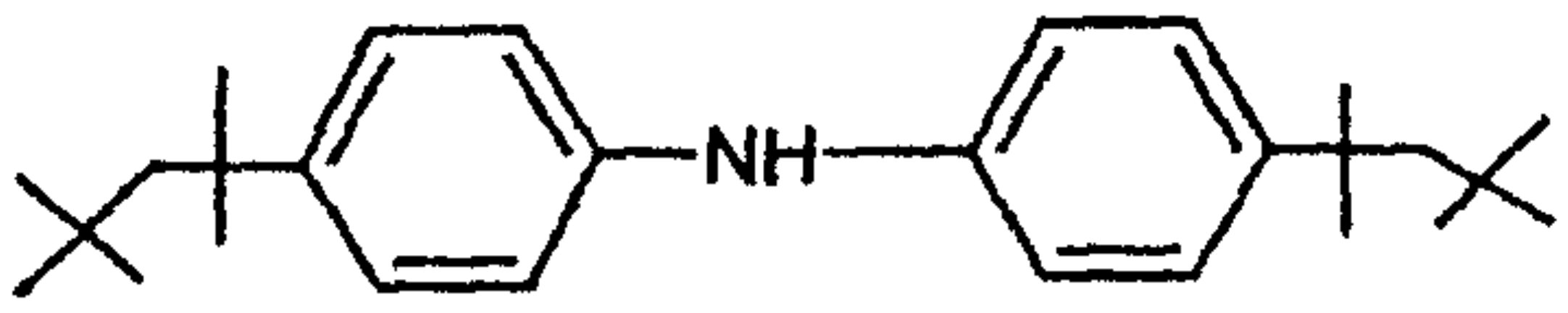
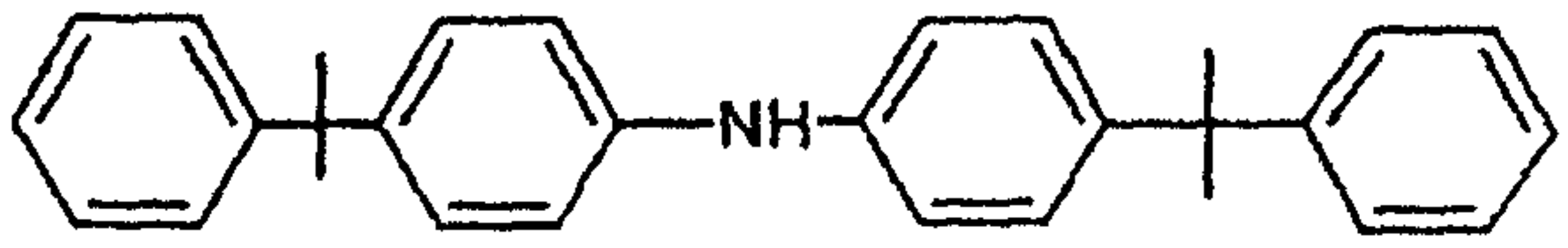
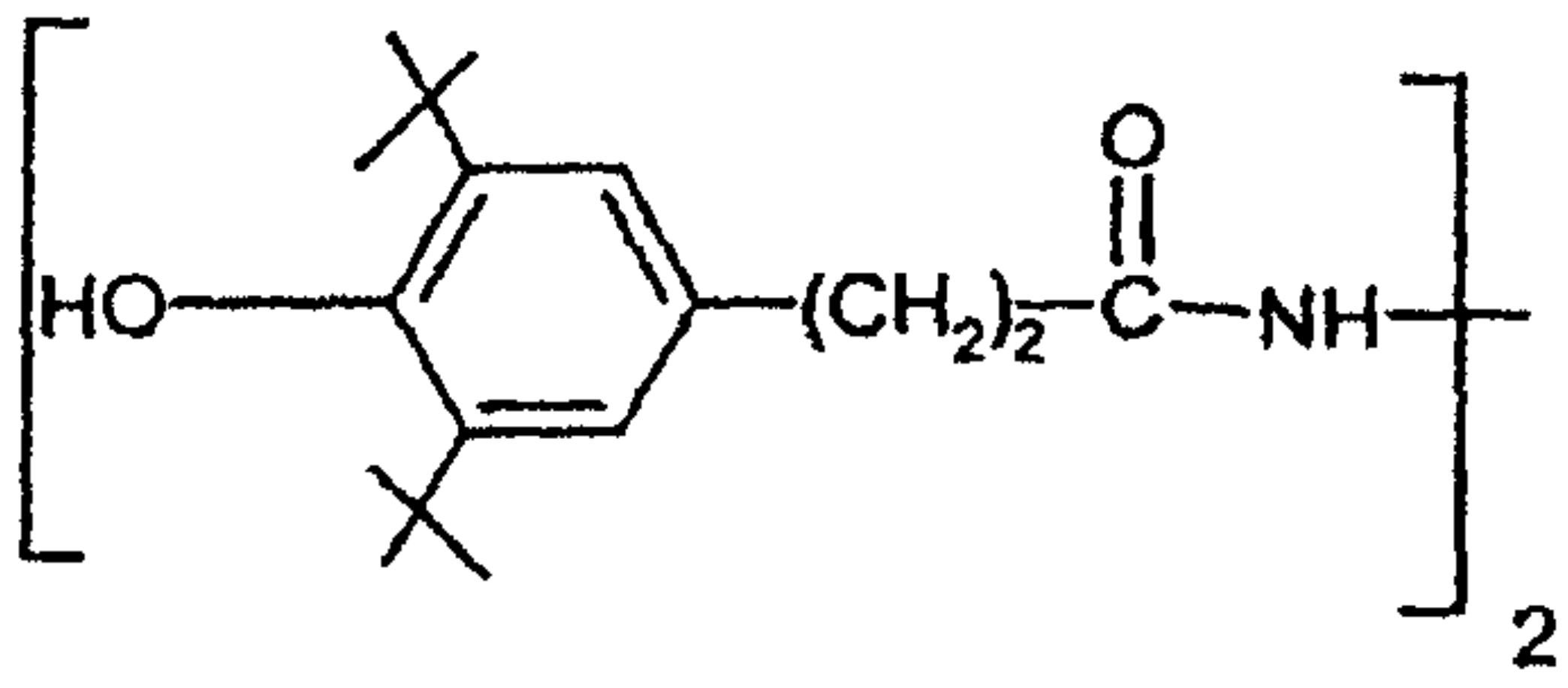
128961-68-2	
135-88-6	
26780-96-1	
101-72-4	
90-30-2	
68411-46-1	
10081-67-1	
32687-78-8	

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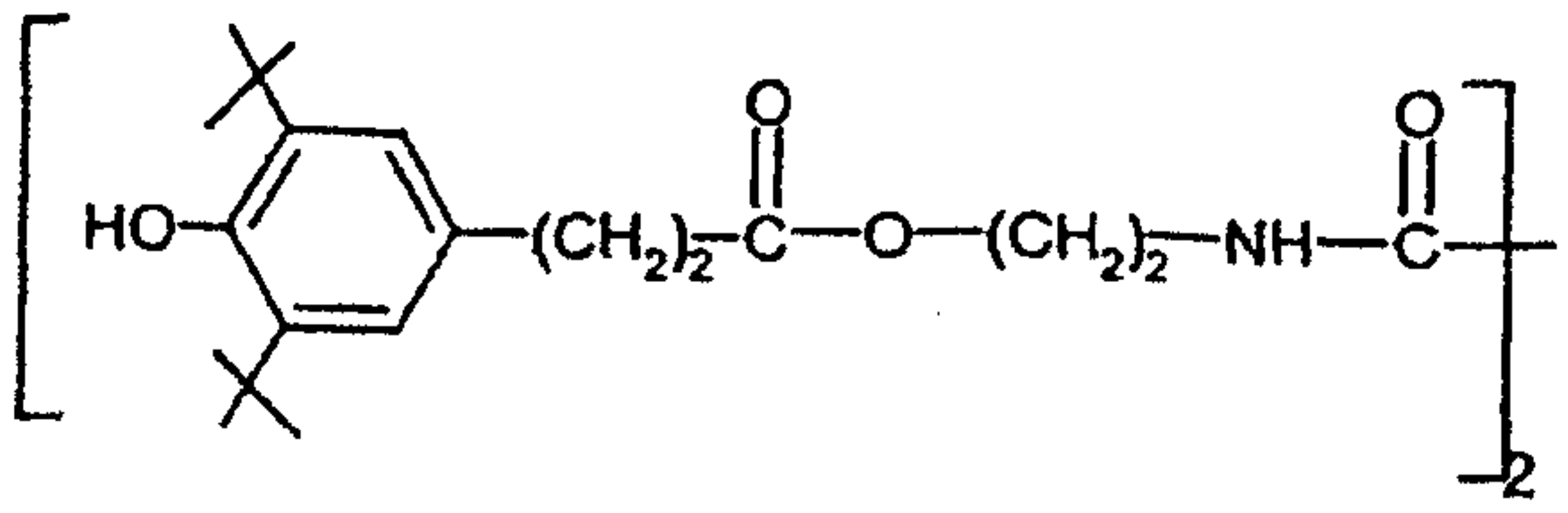
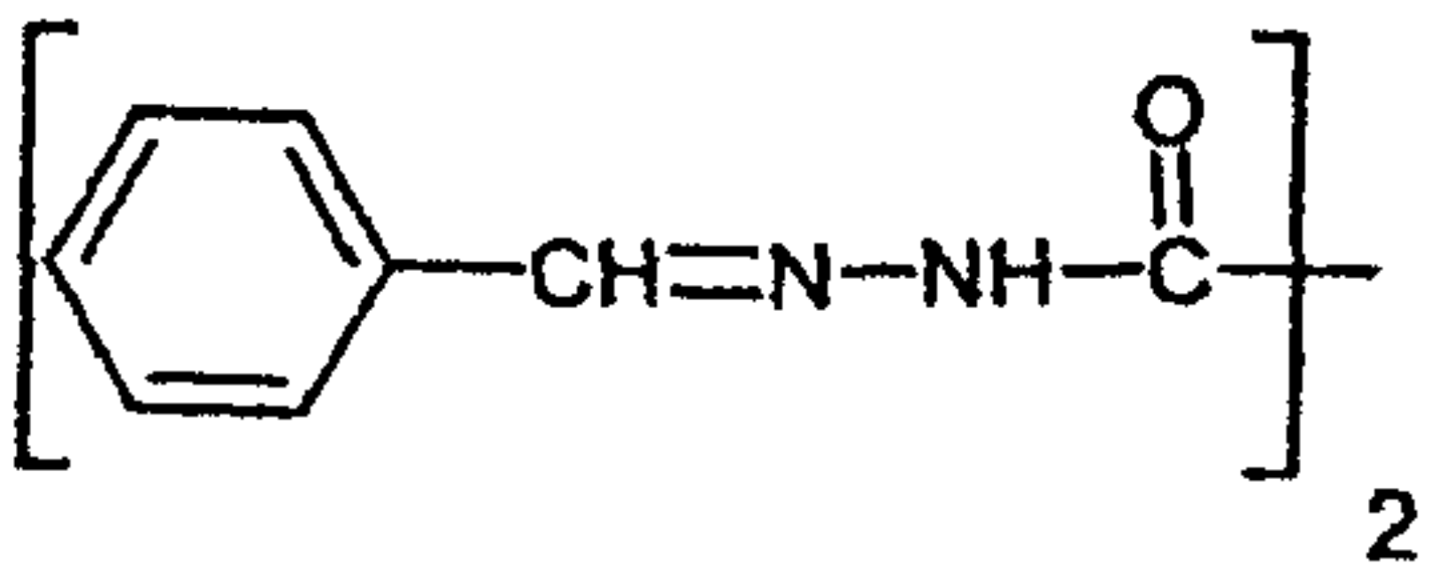
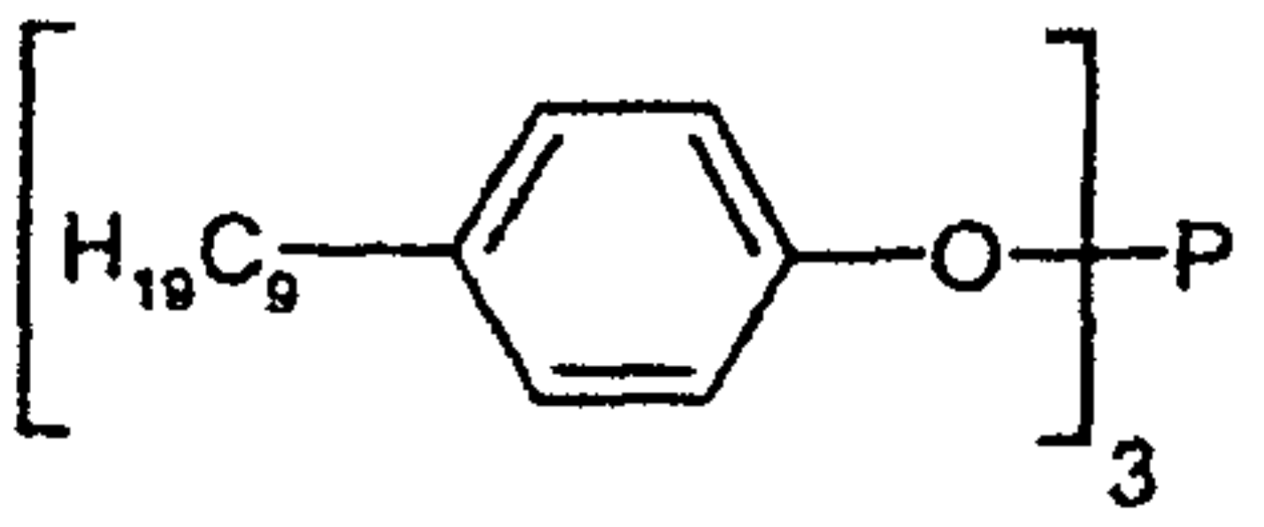
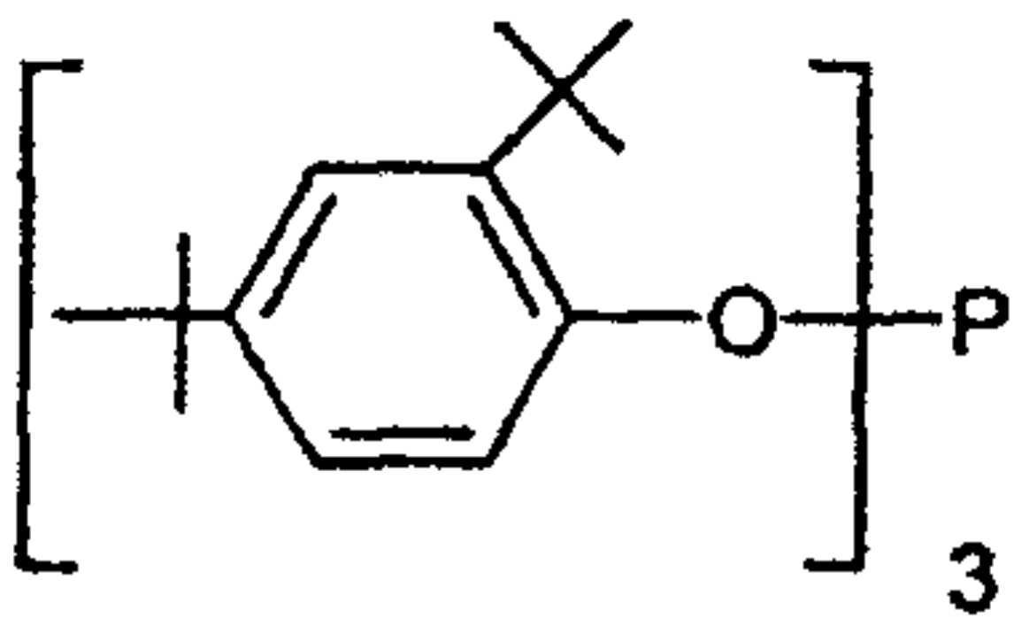
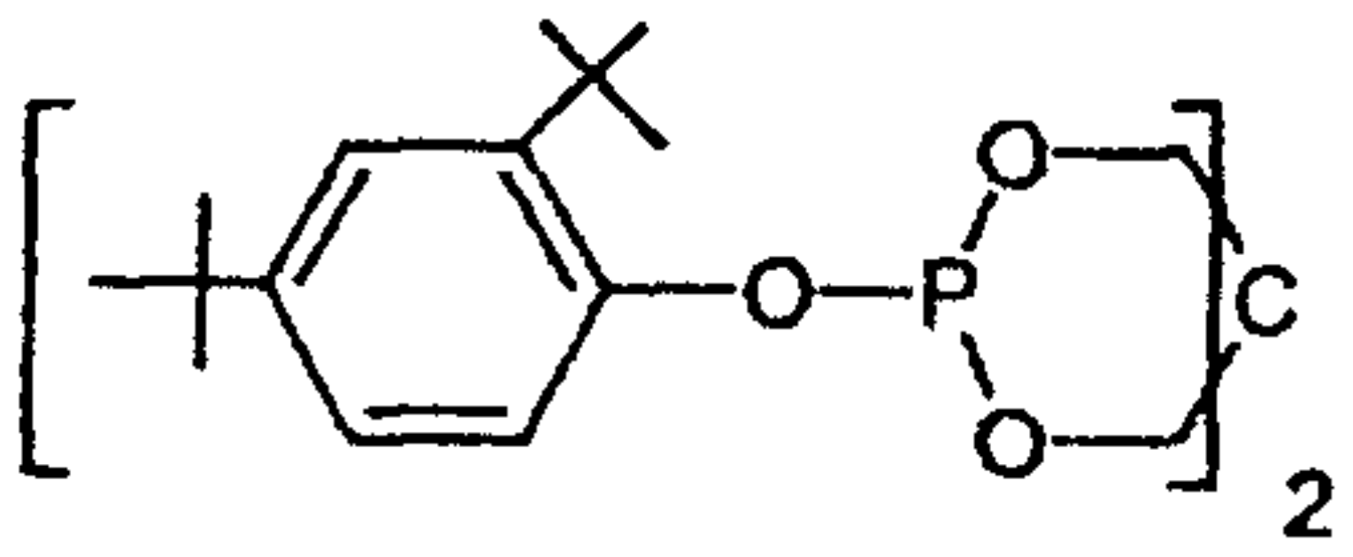
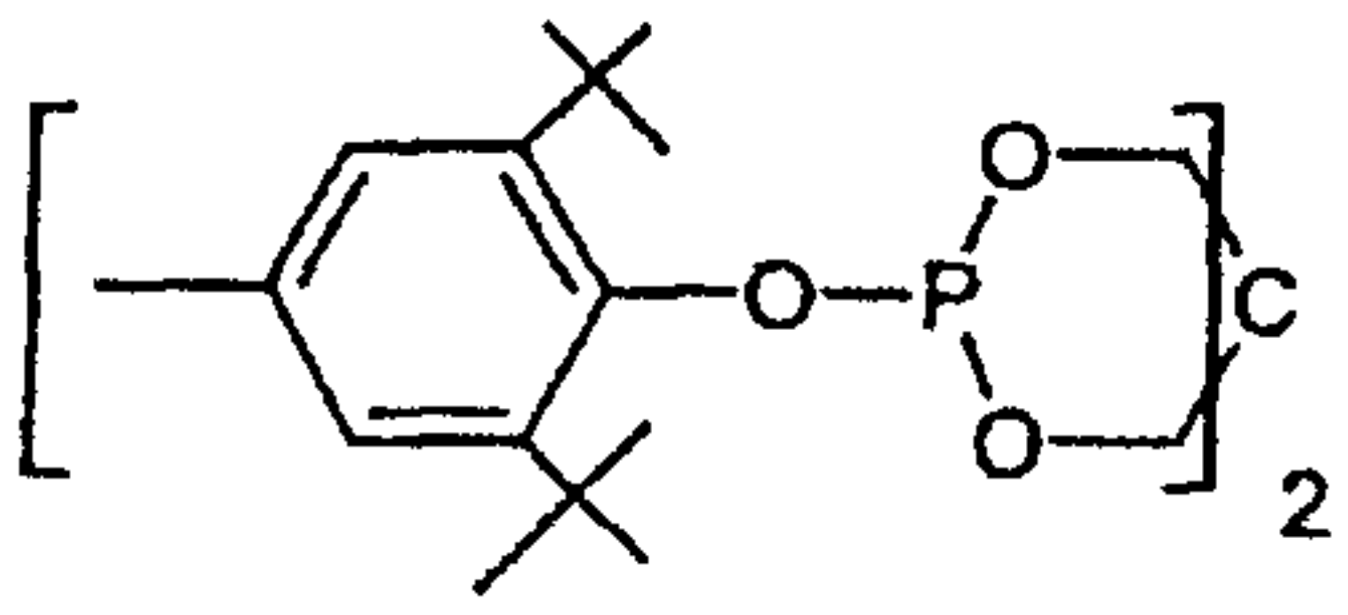
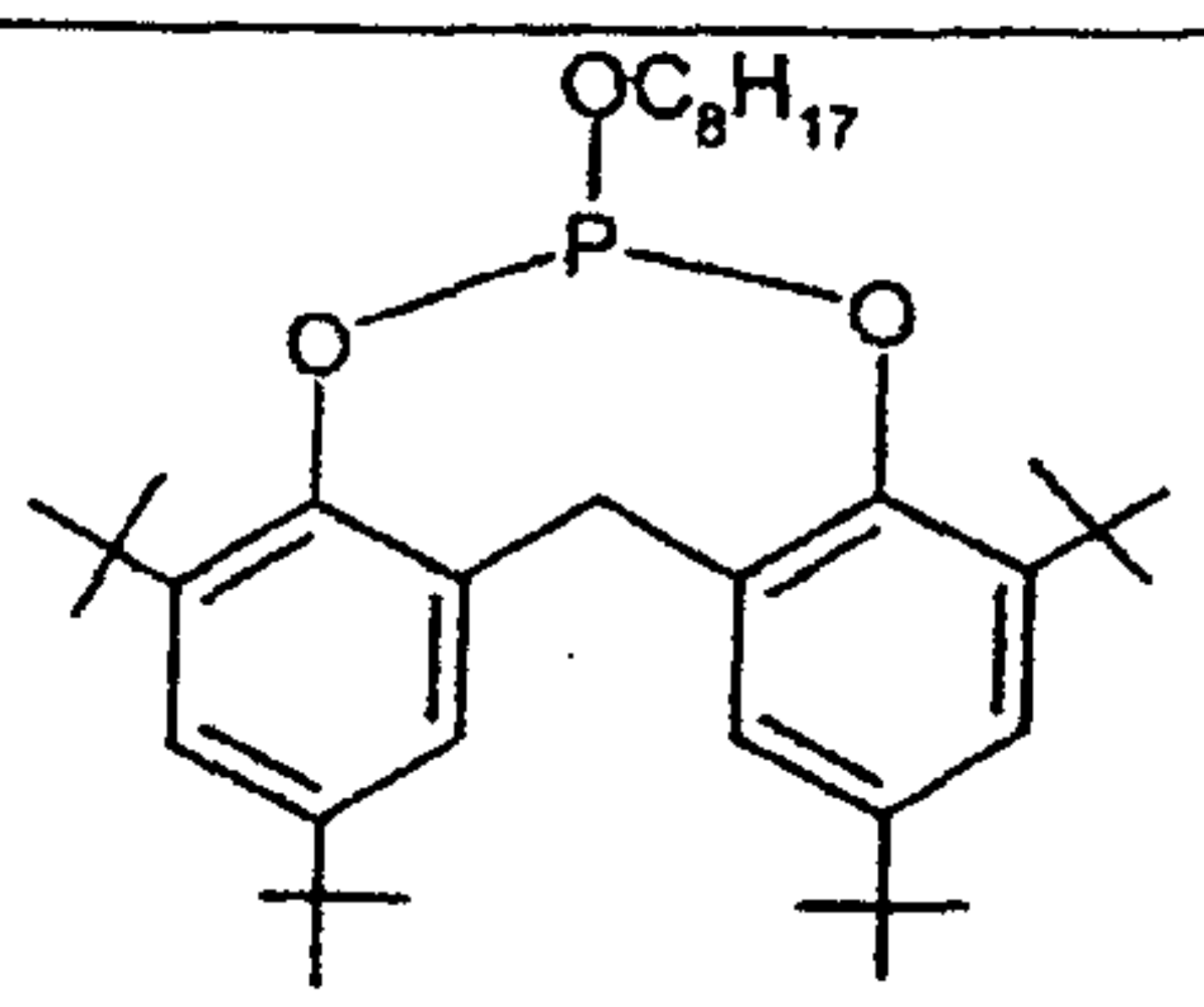
70331-94-1	
6629-10-3	
26523-78-4	
31570-04-4	
26741-53-7	
80693-00-1	
140221-14-3	

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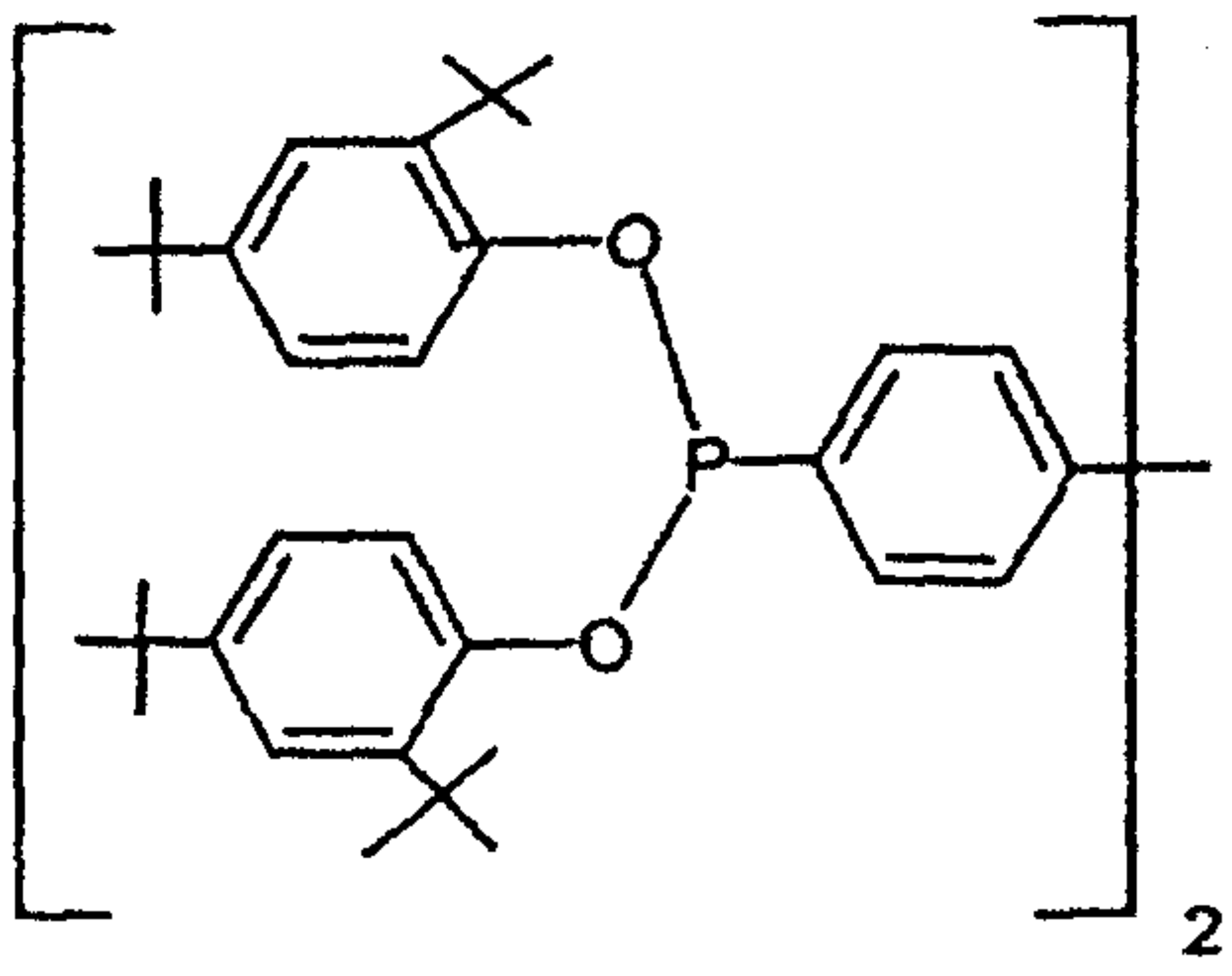
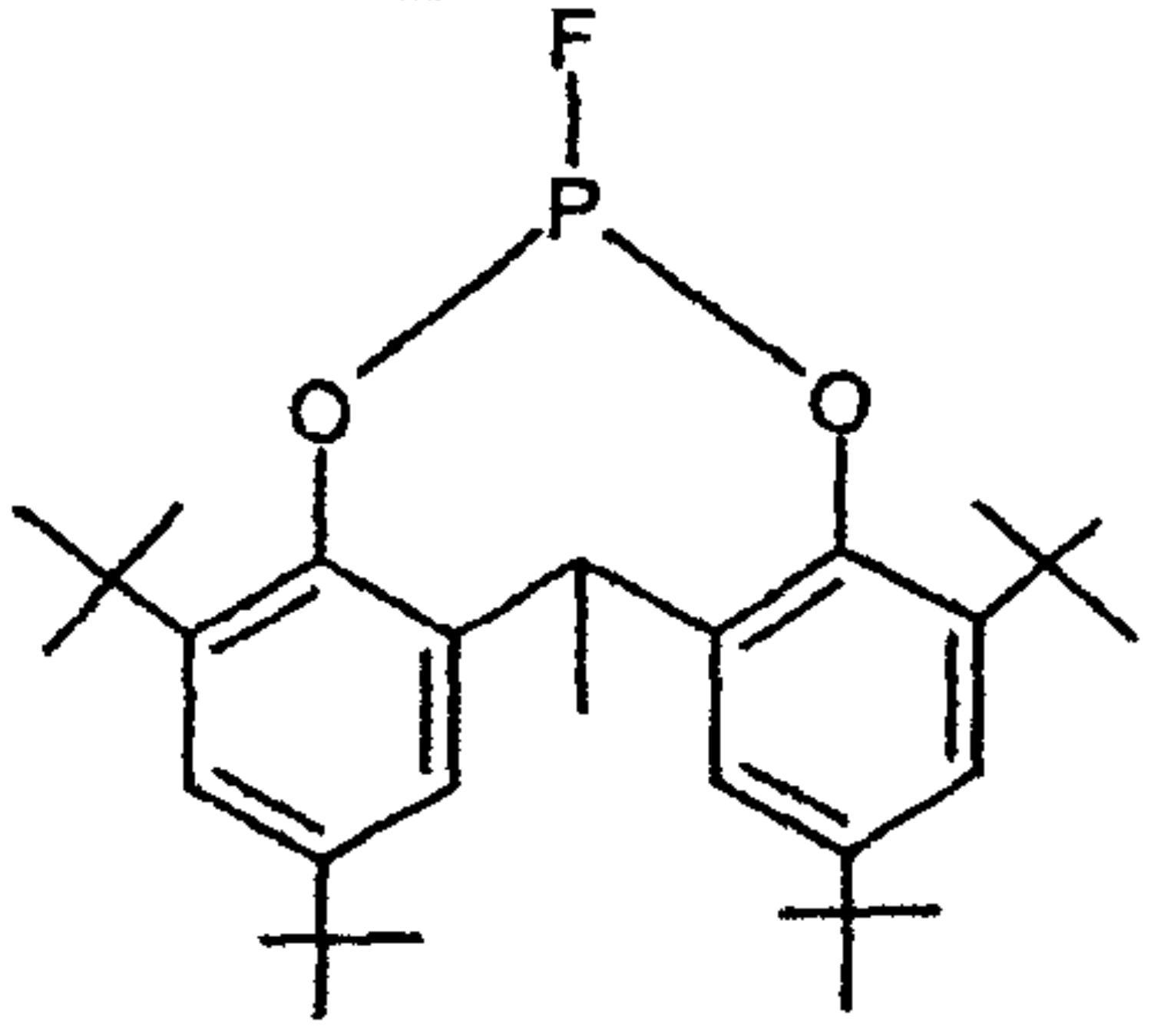
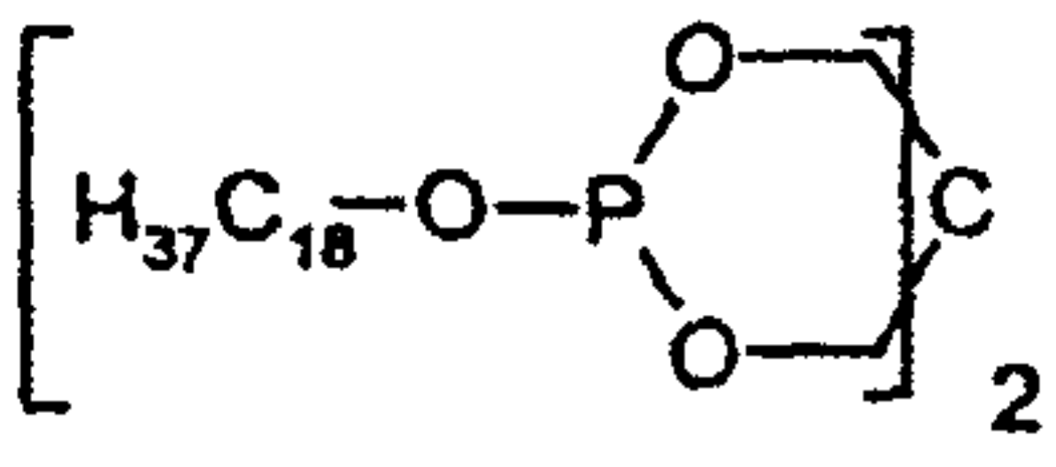
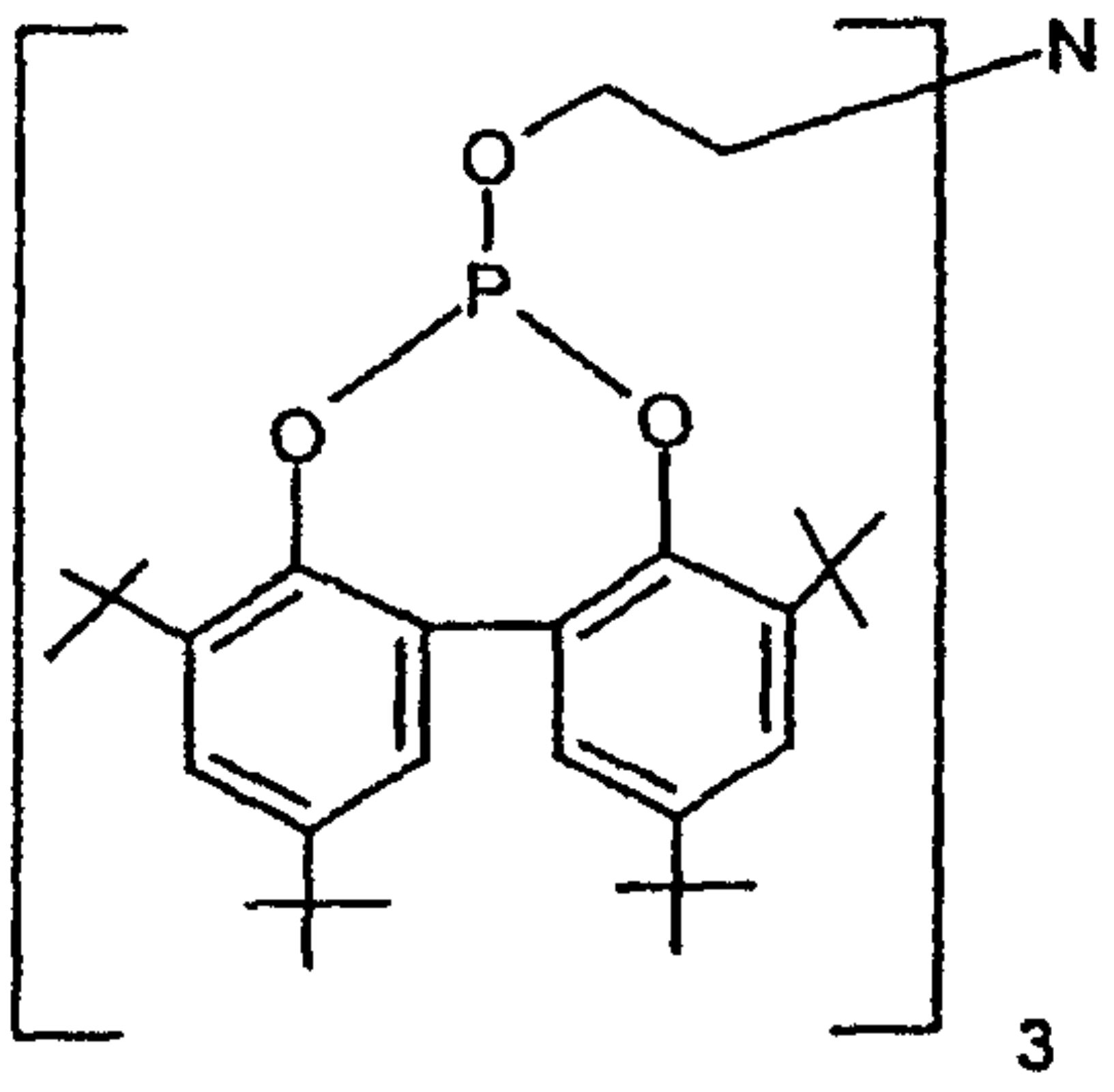
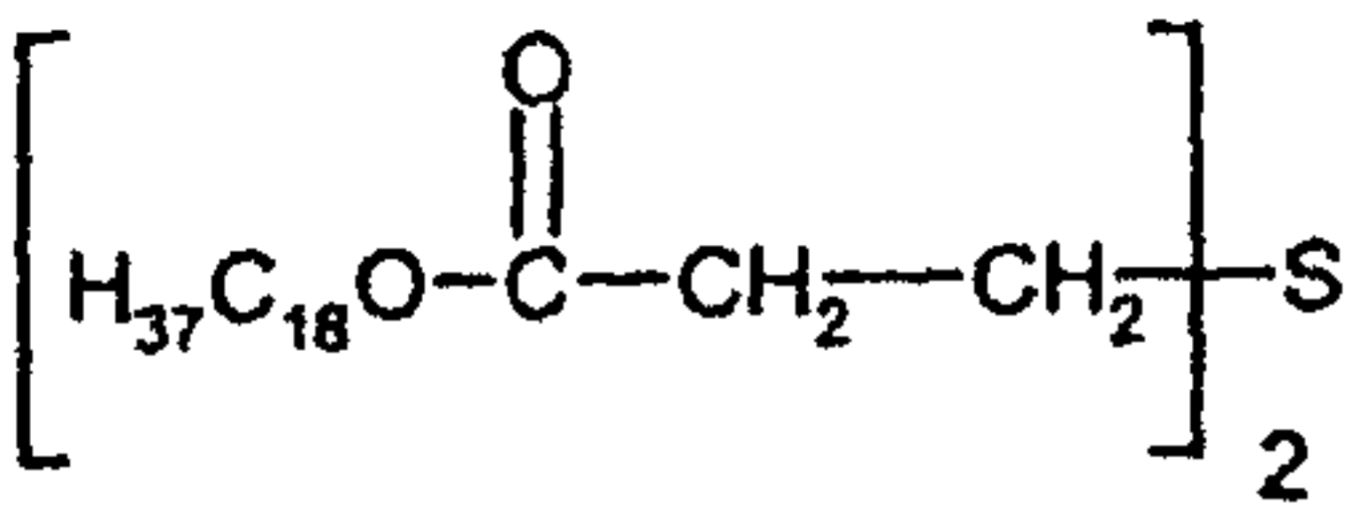
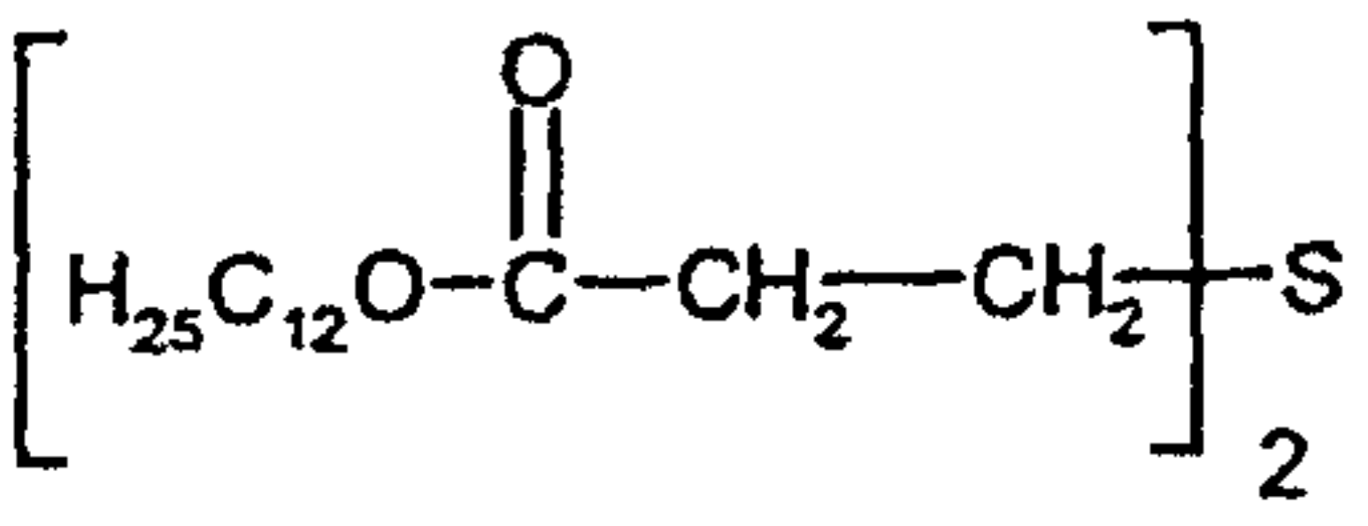
38613-77-3	
118337-09-0	
3806-34-6	
80410-33-9	
693-36-7	 $\left[H_{37}C_{18}O-\overset{\overset{\displaystyle O}{\|}}{C}-CH_2-CH_2\right]_2S$
123-28-4	 $\left[H_{25}C_{12}O-\overset{\overset{\displaystyle O}{\|}}{C}-CH_2-CH_2\right]_2S$

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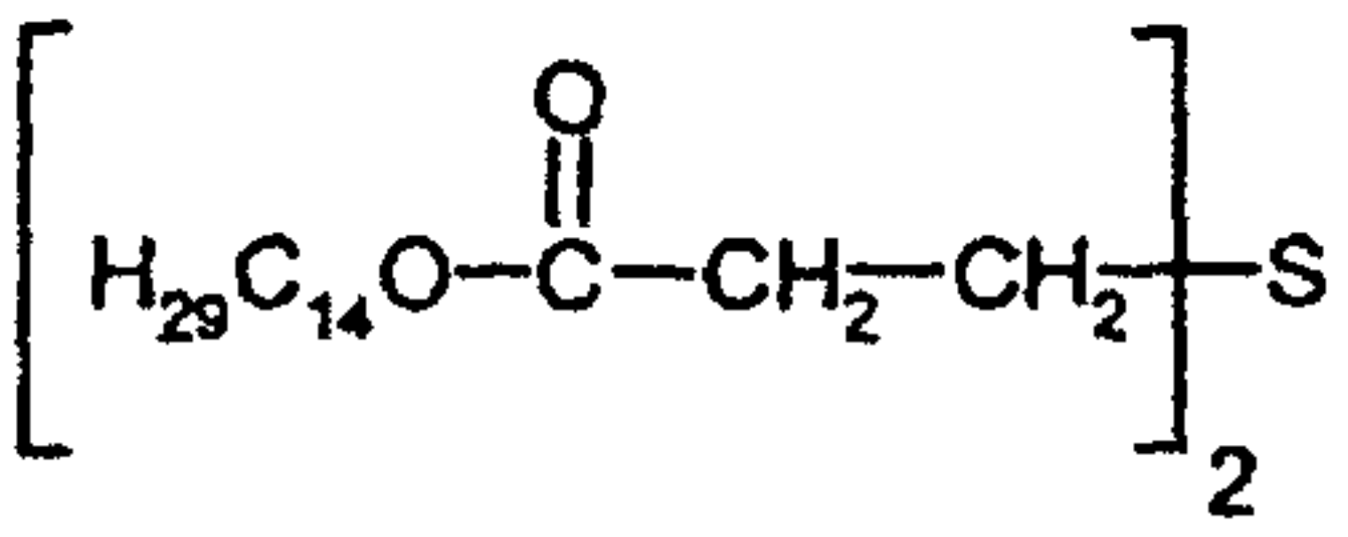
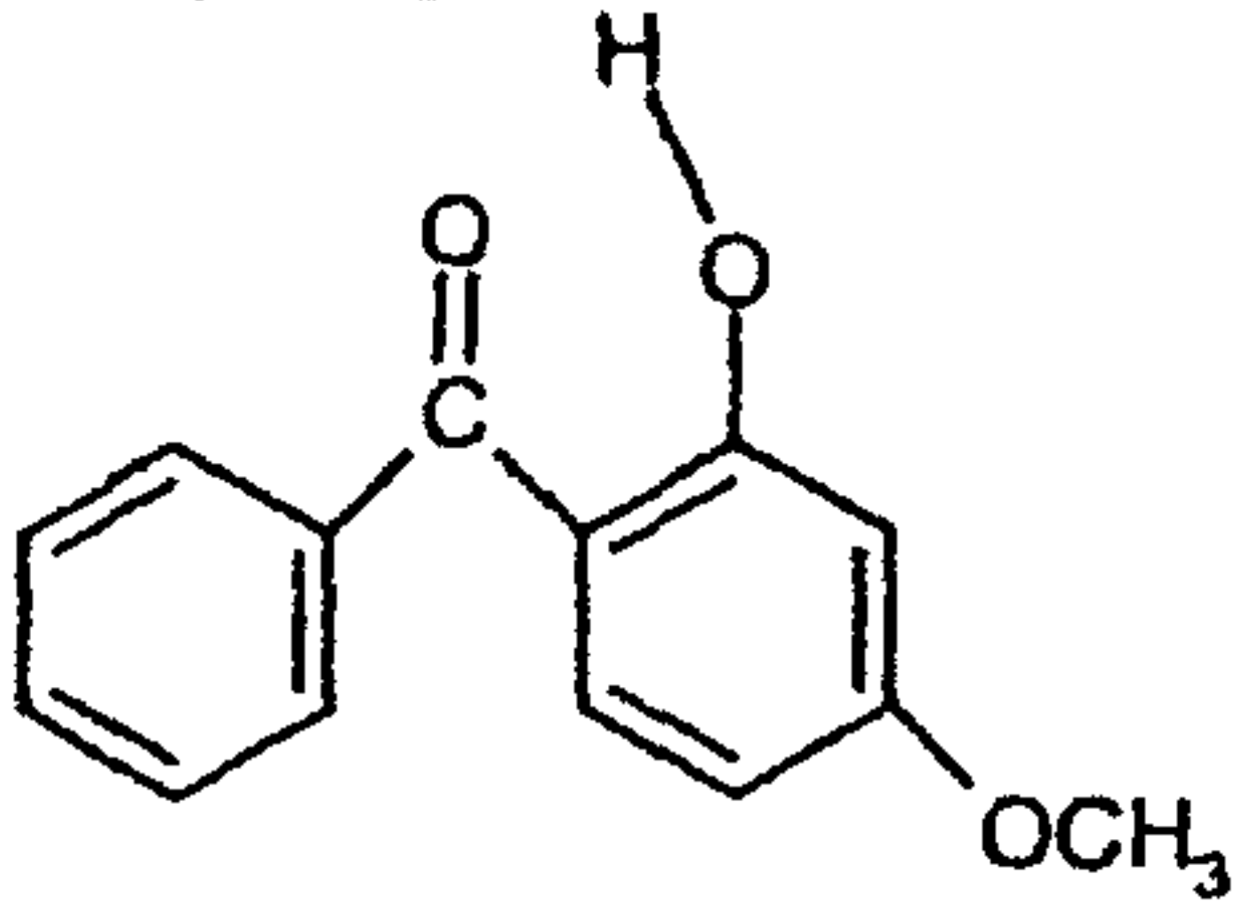
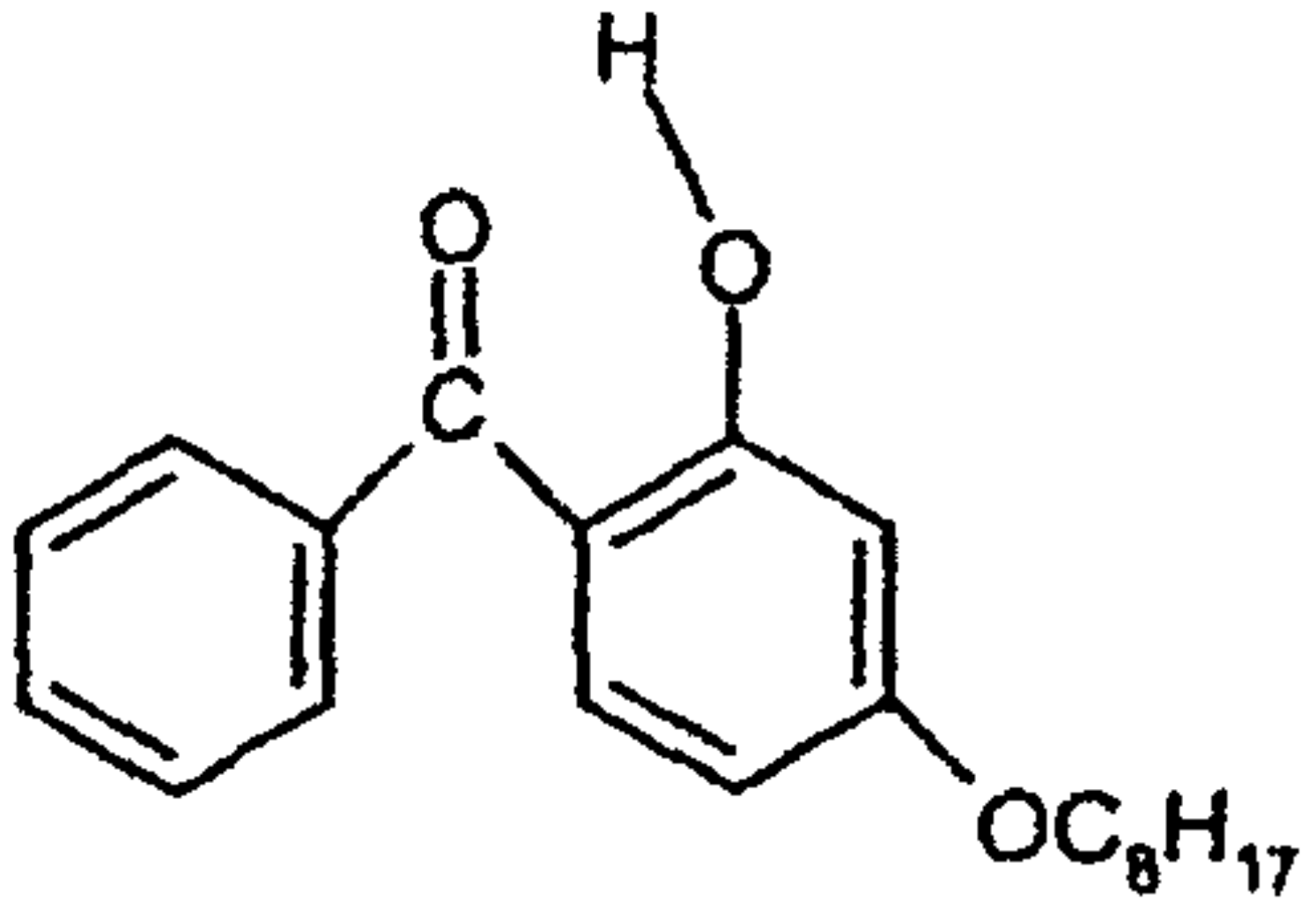
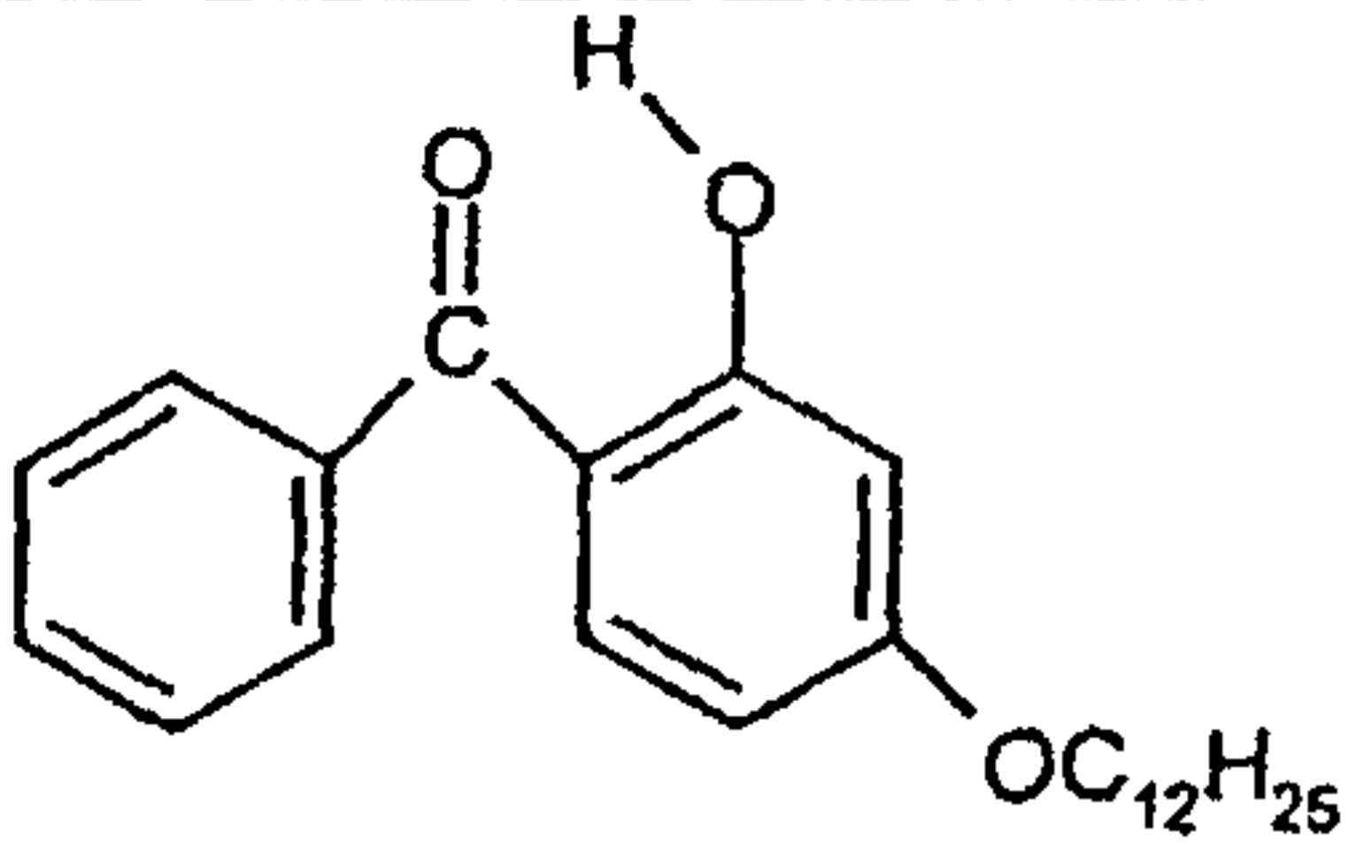
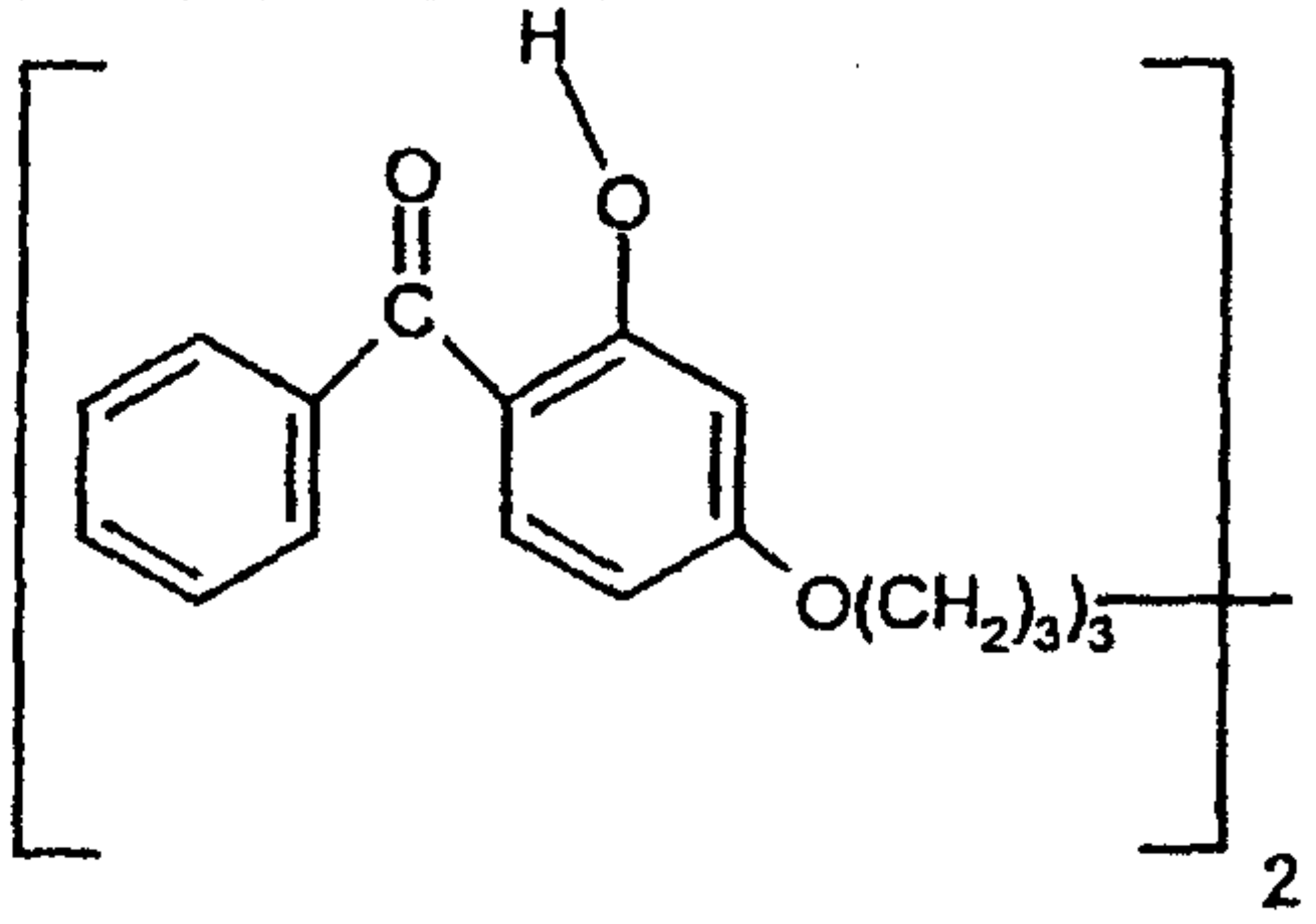
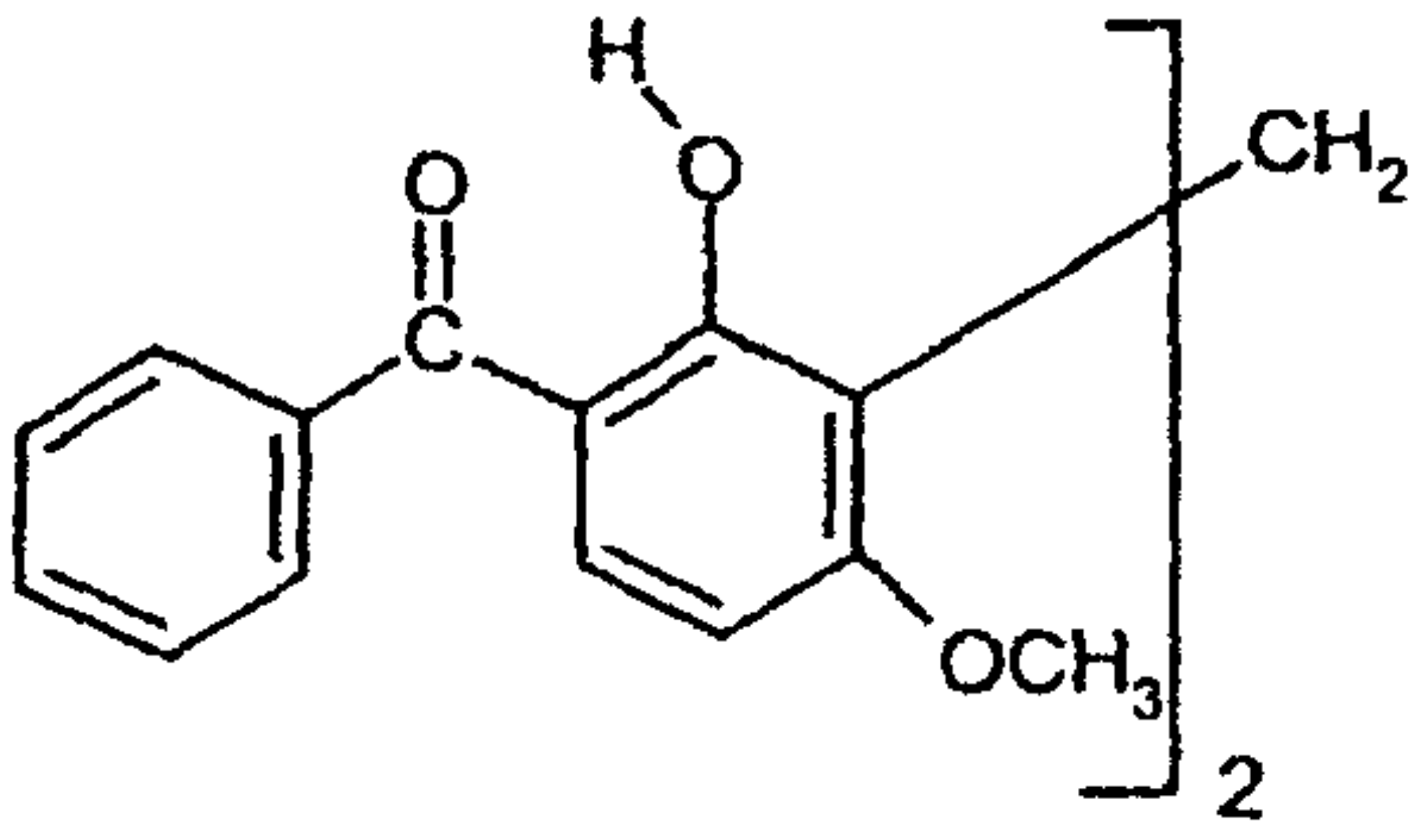
16545-54-3	 $\left[H_{29}C_{14}O-\overset{\displaystyle O}{\overset{\Vert}{C}}-CH_2-CH_2\right]_2 S$
2500-88-1	$\left[H_{37}C_{18}-S-\right]_2$
131-57-7	
1843-05-6	
2985-59-3	
43221-33-6	
57472-50-1	

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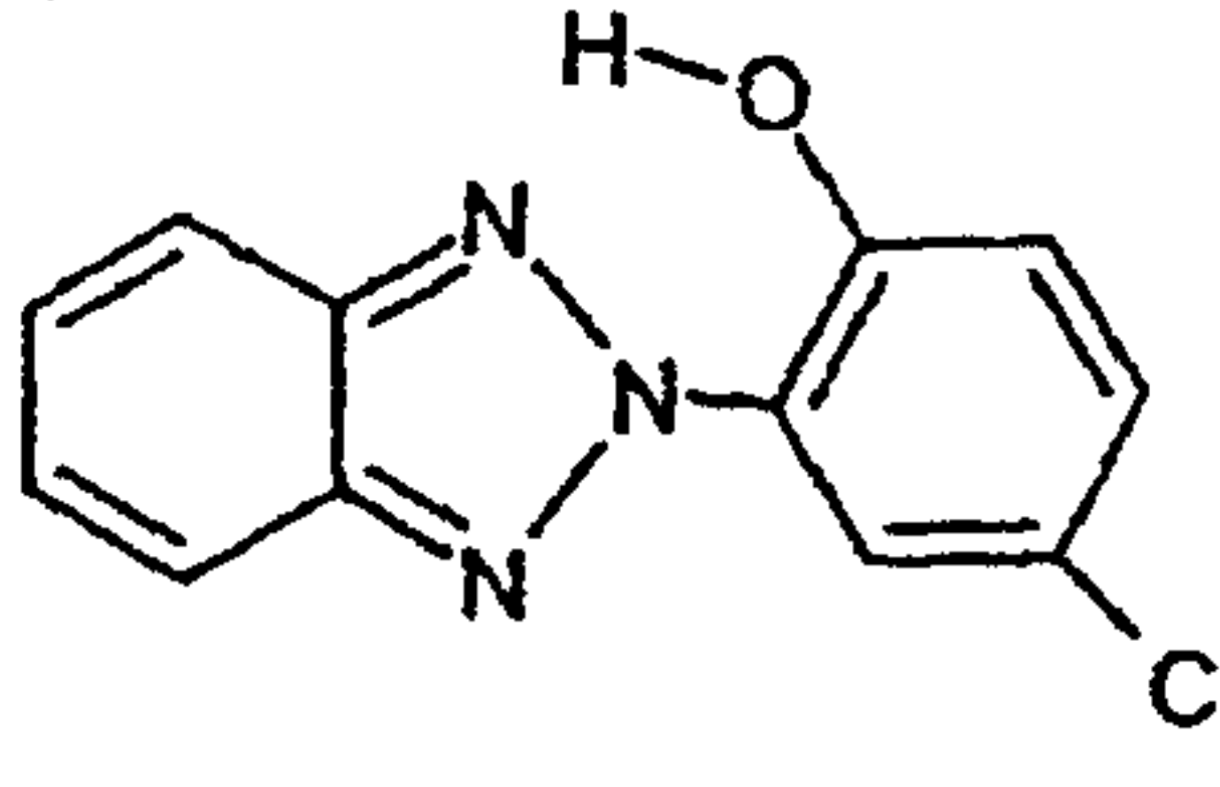
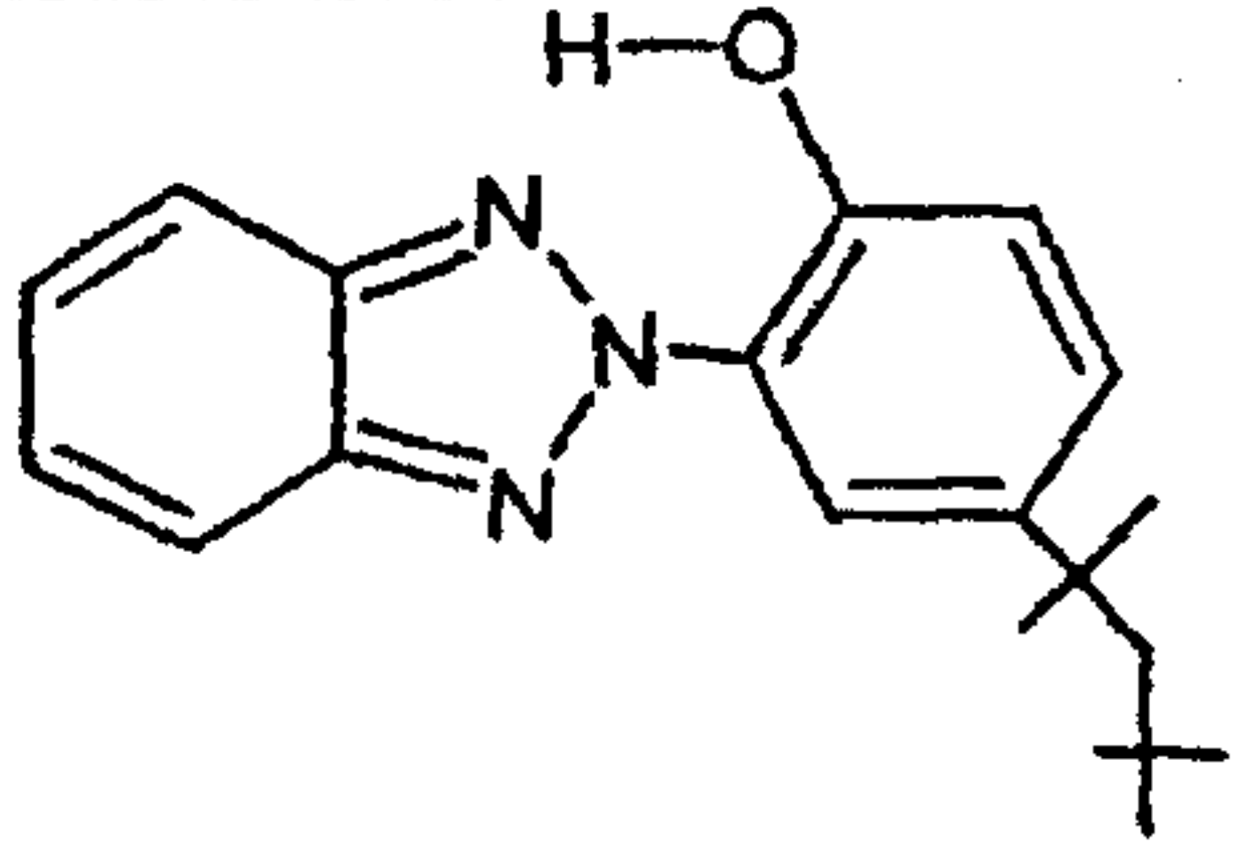
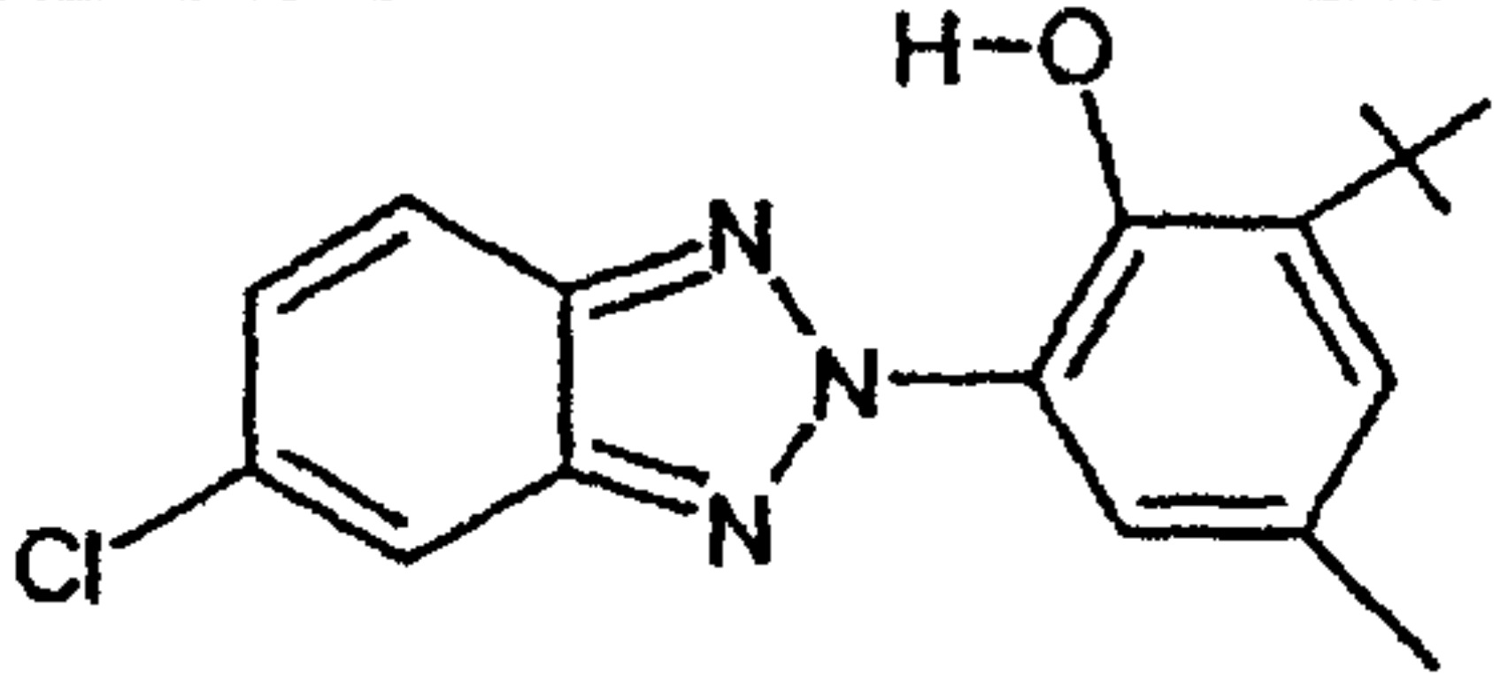
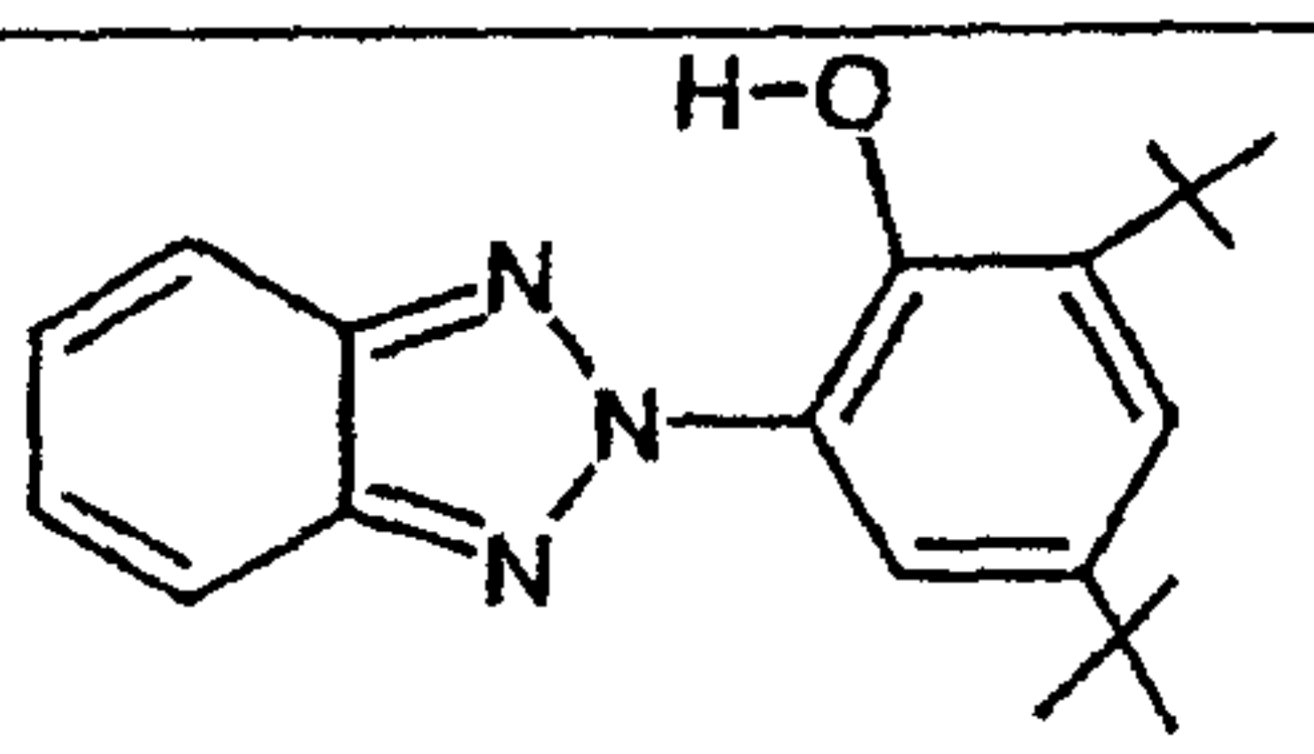
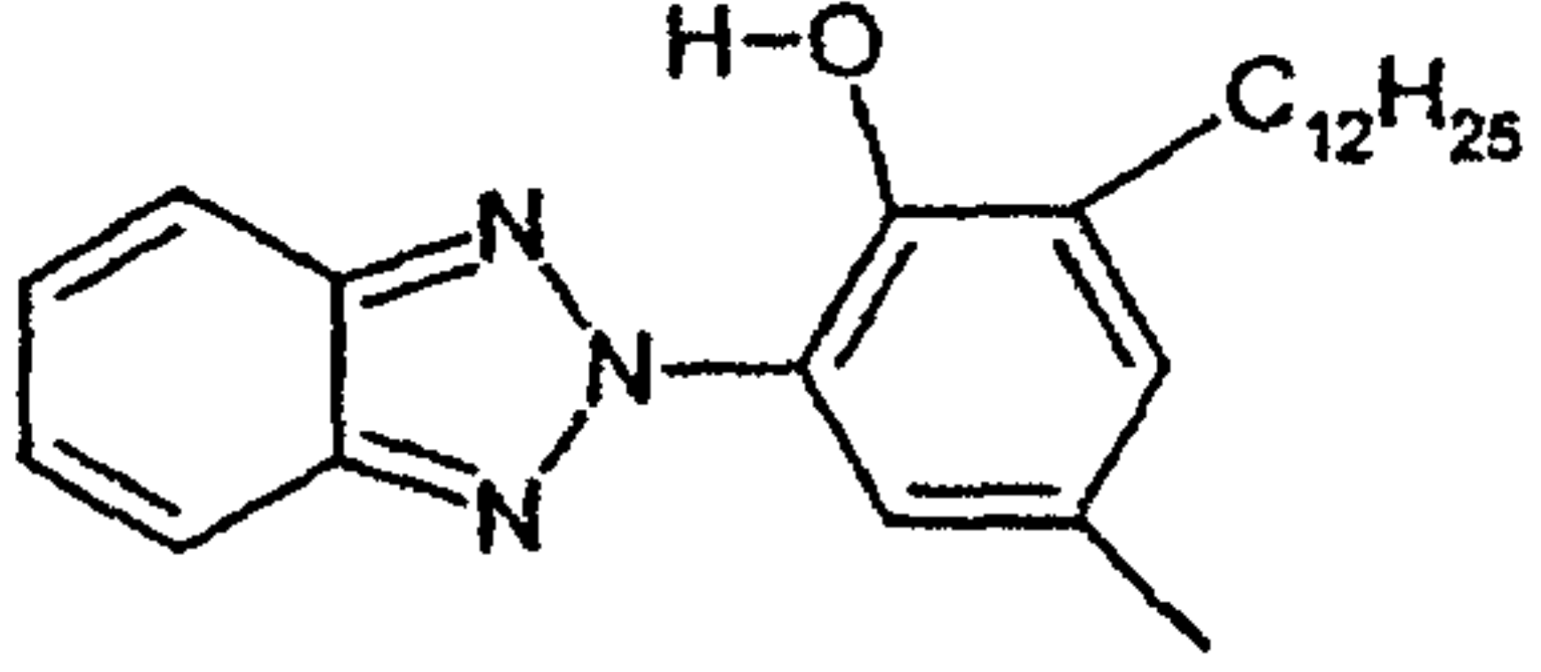
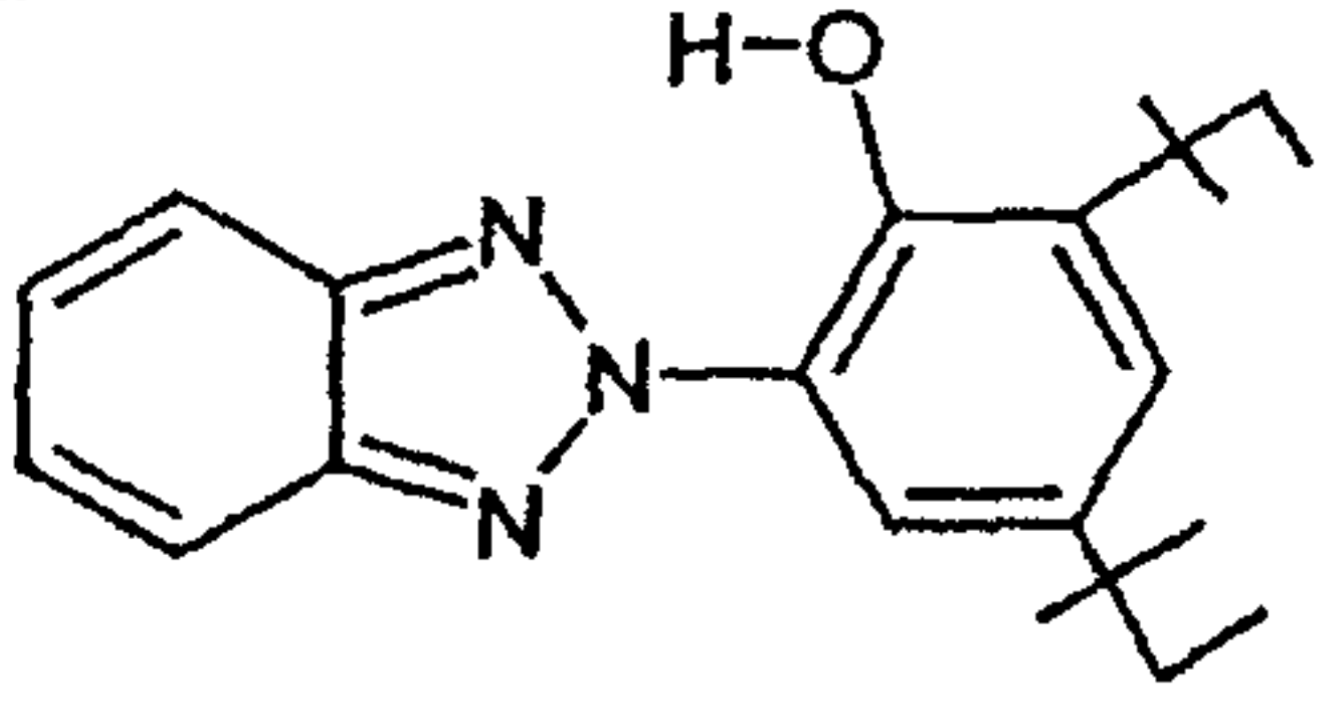
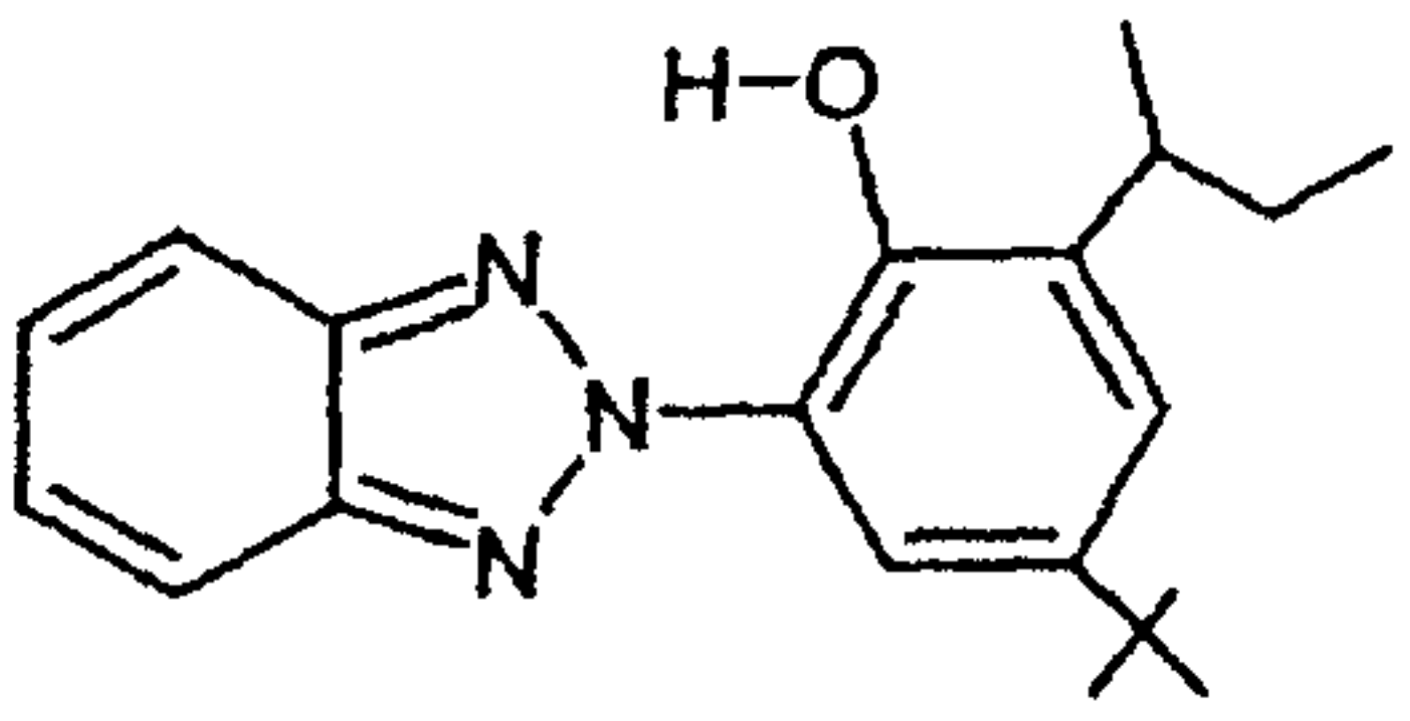
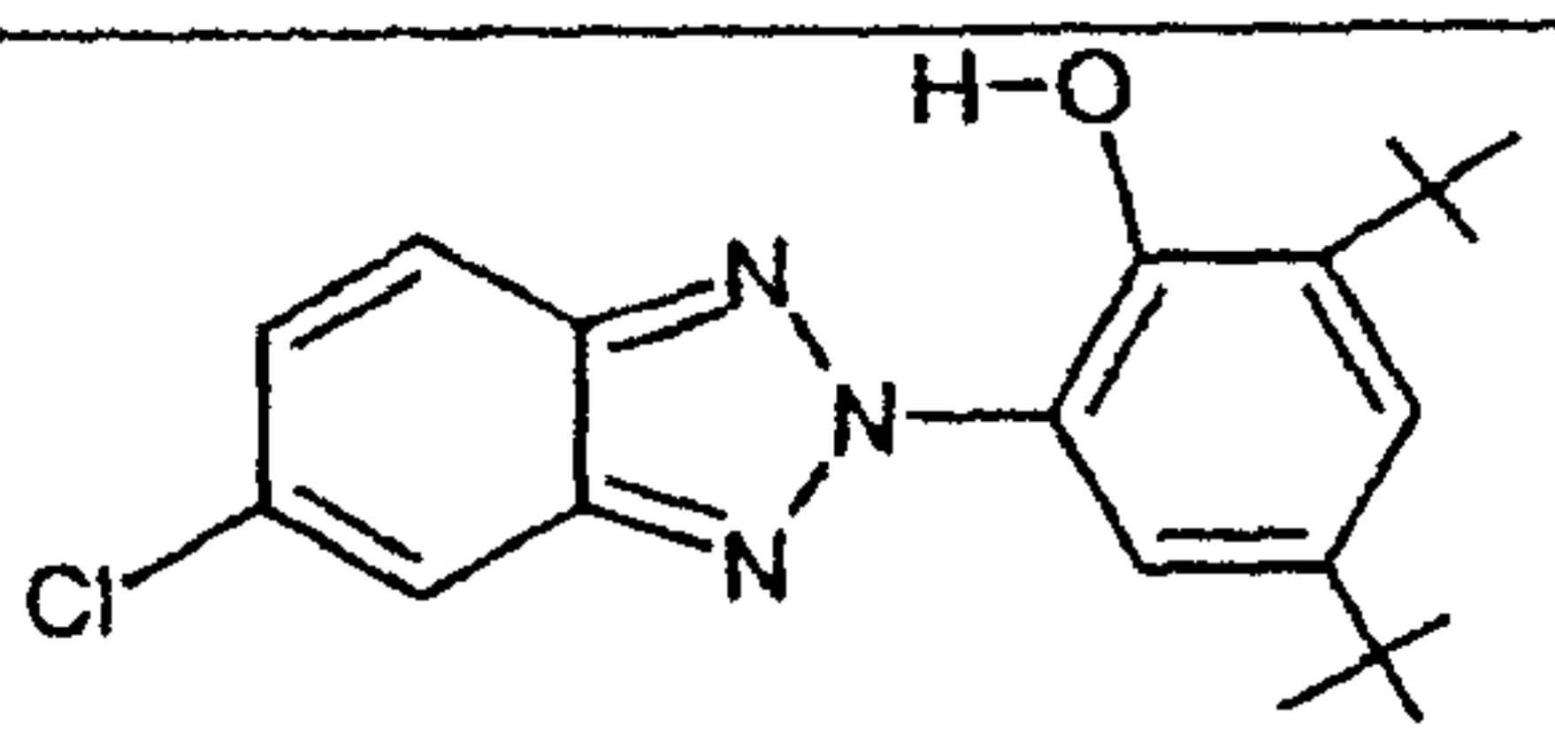
2440-22-4	
3147-75-9	
3896-11-5	
3846-71-7	
23328-53-2	
25973-55-1	
36437-37-3	
3864-99-1	

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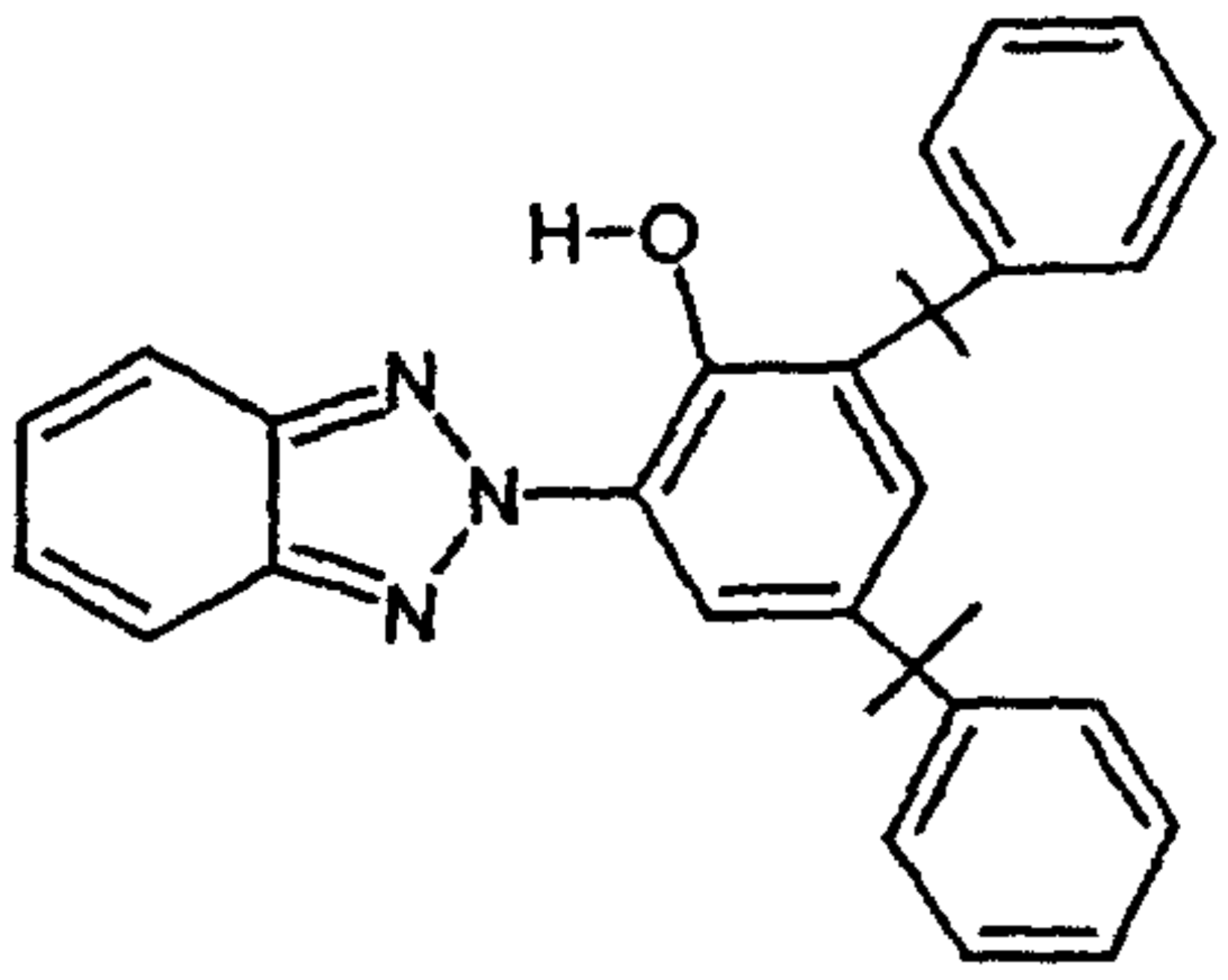
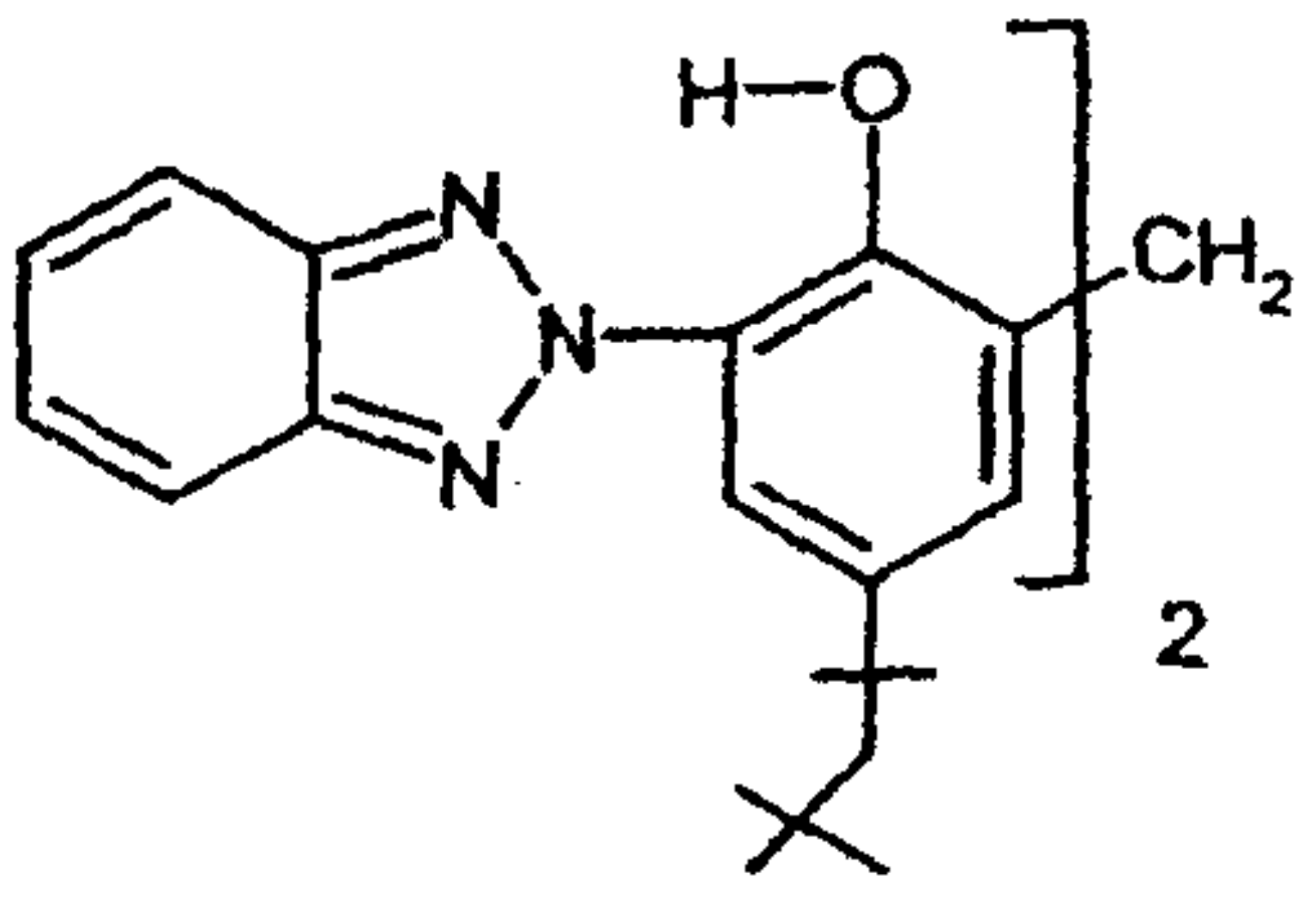
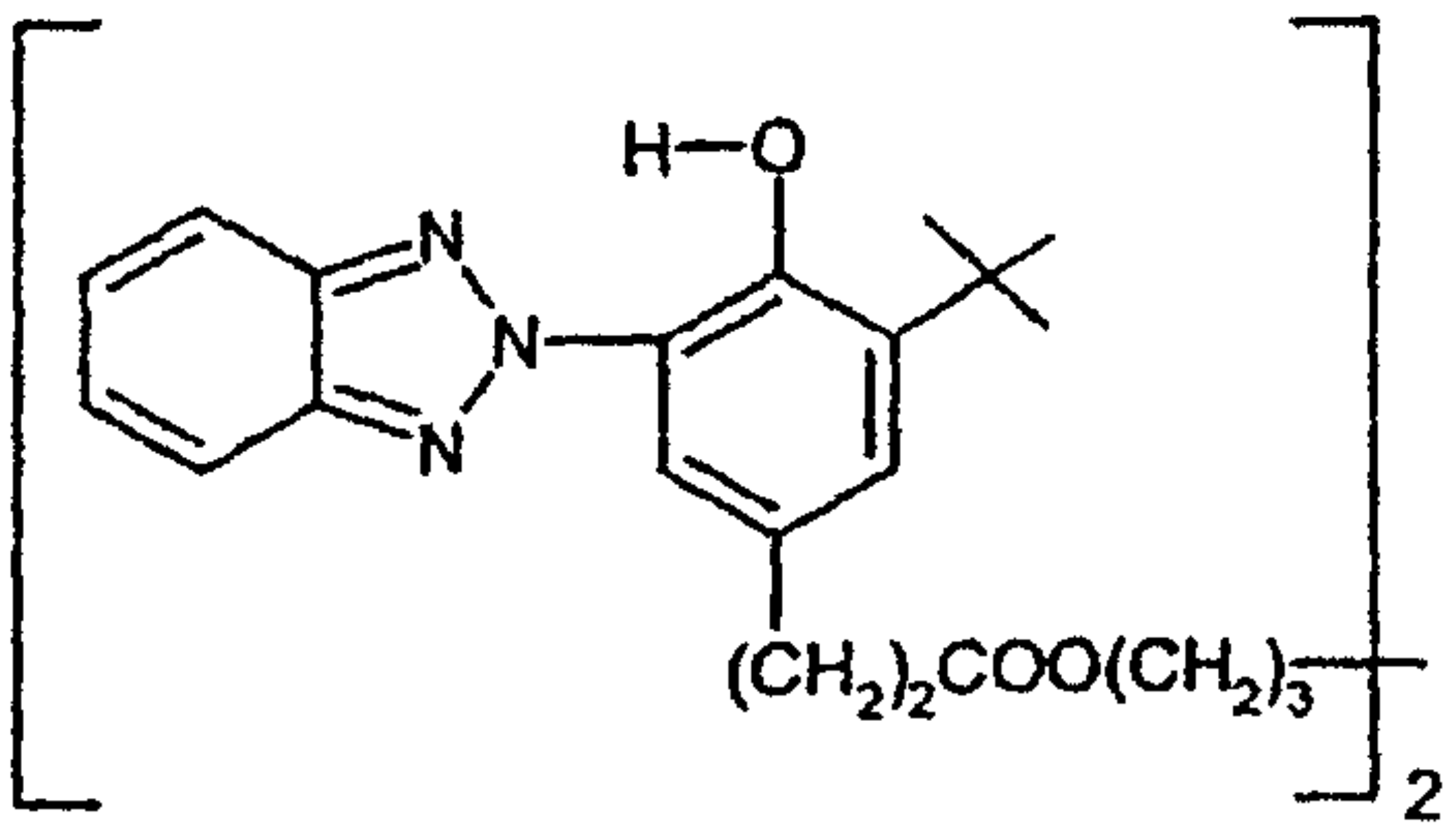
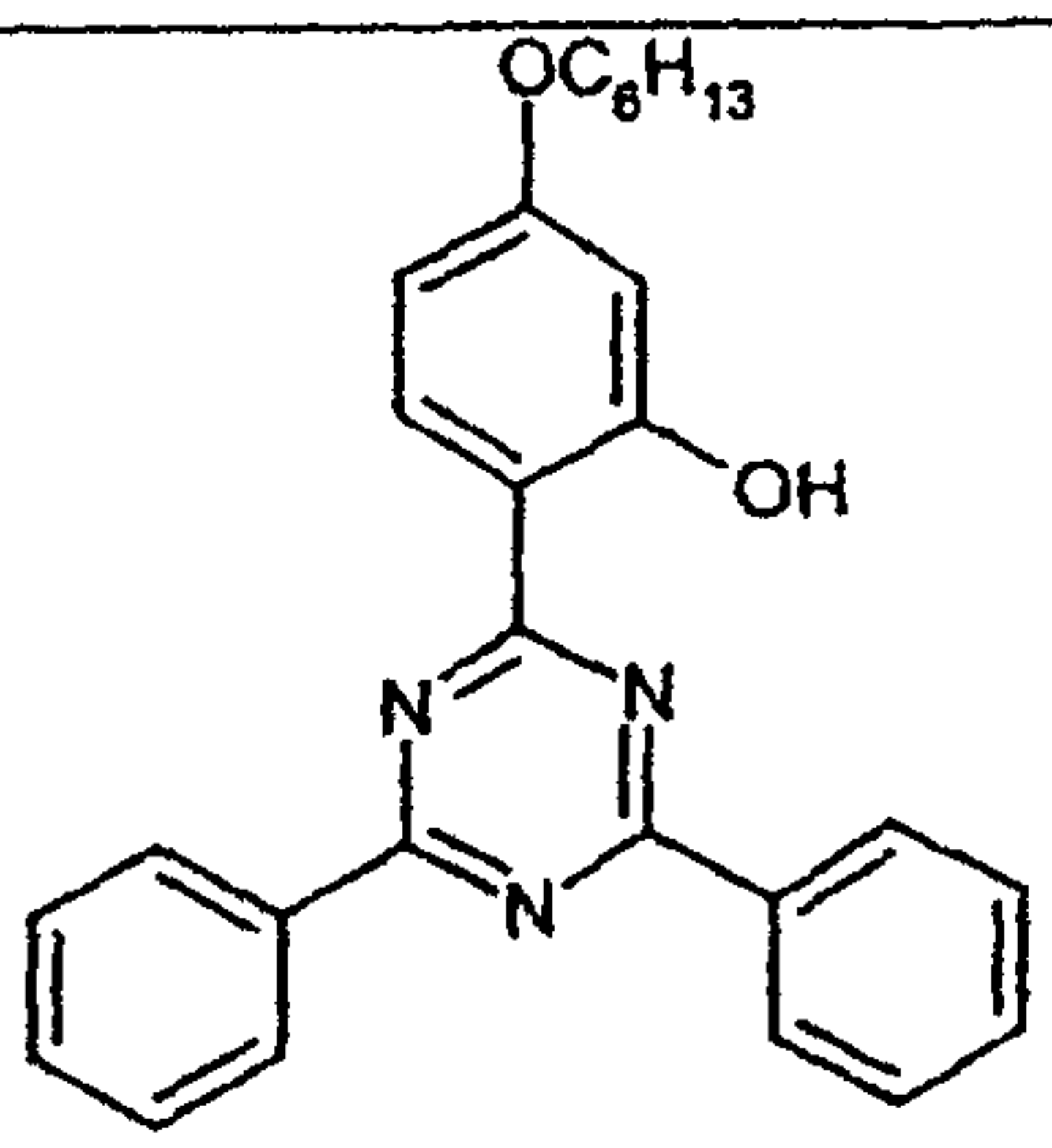
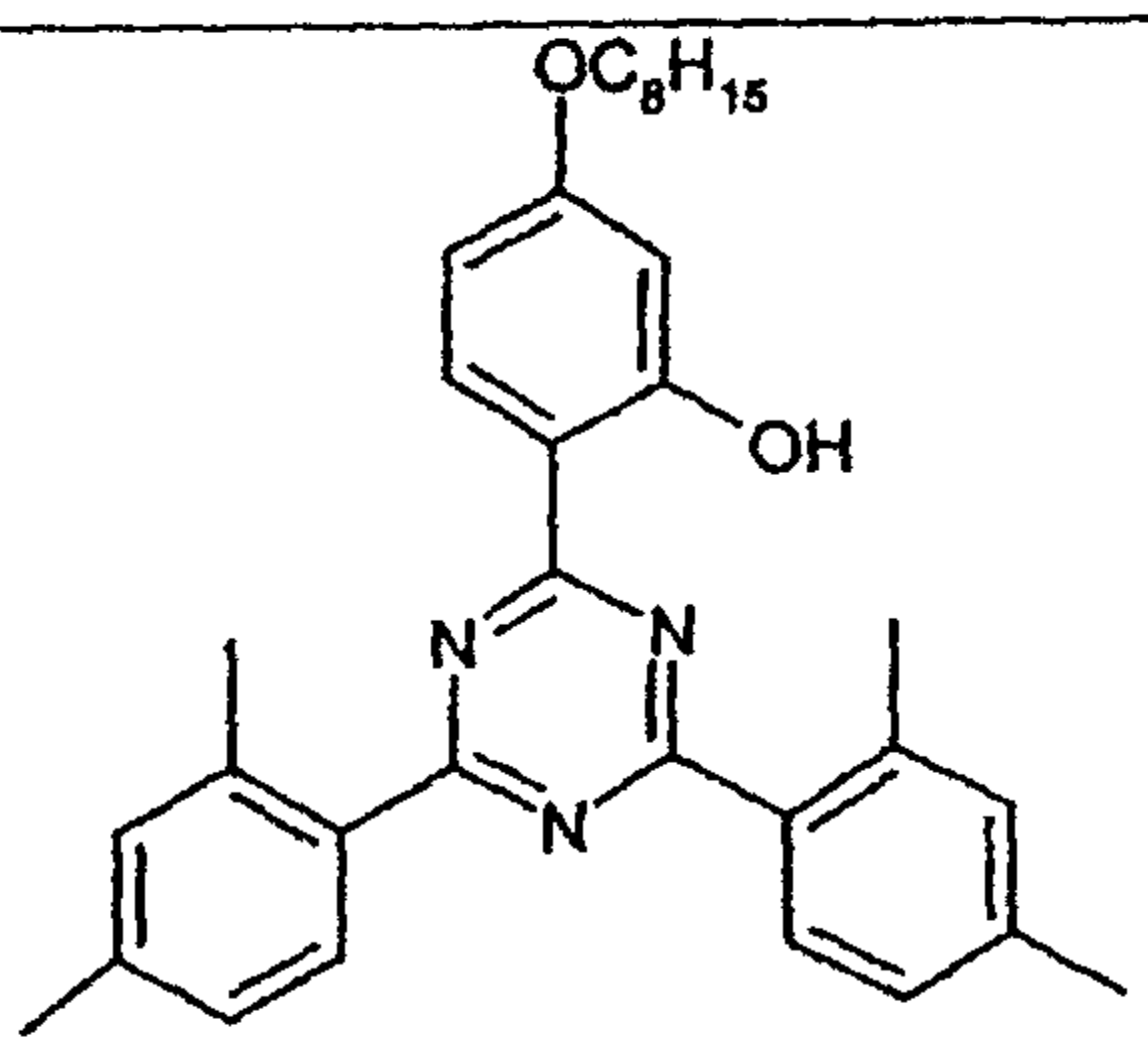
70321-86-7	
103597-45-1	
84268-08-6	
147315-50-2	
2725-22-6	

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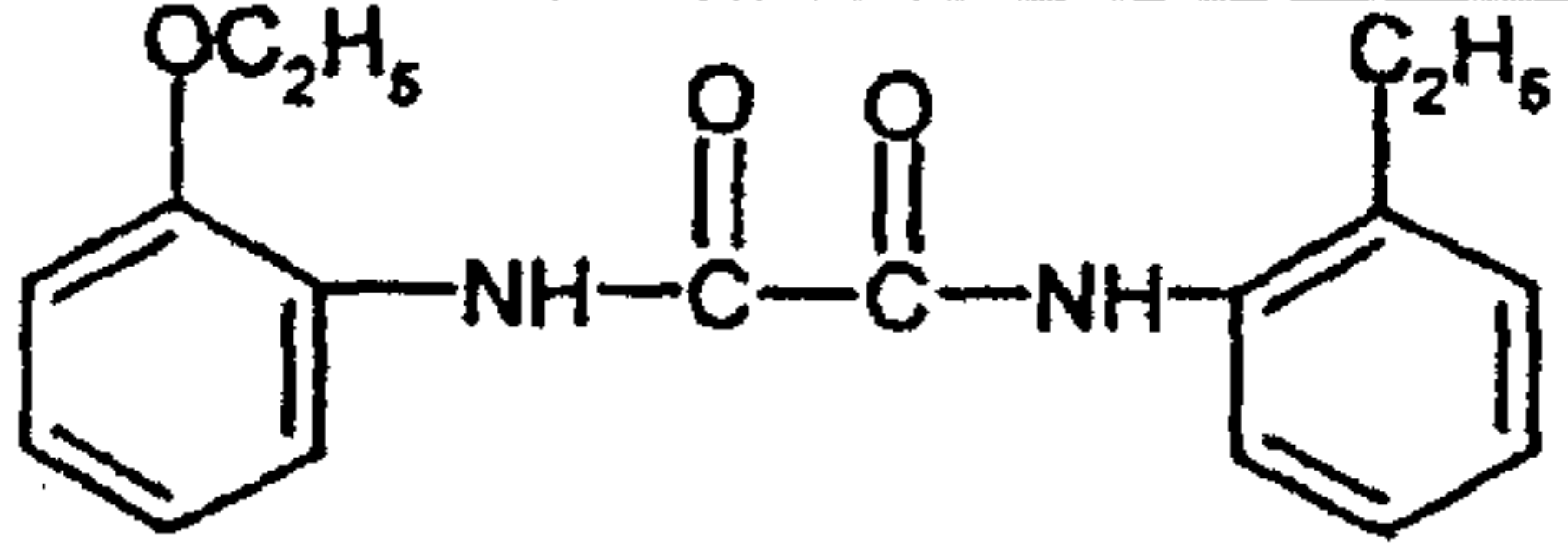
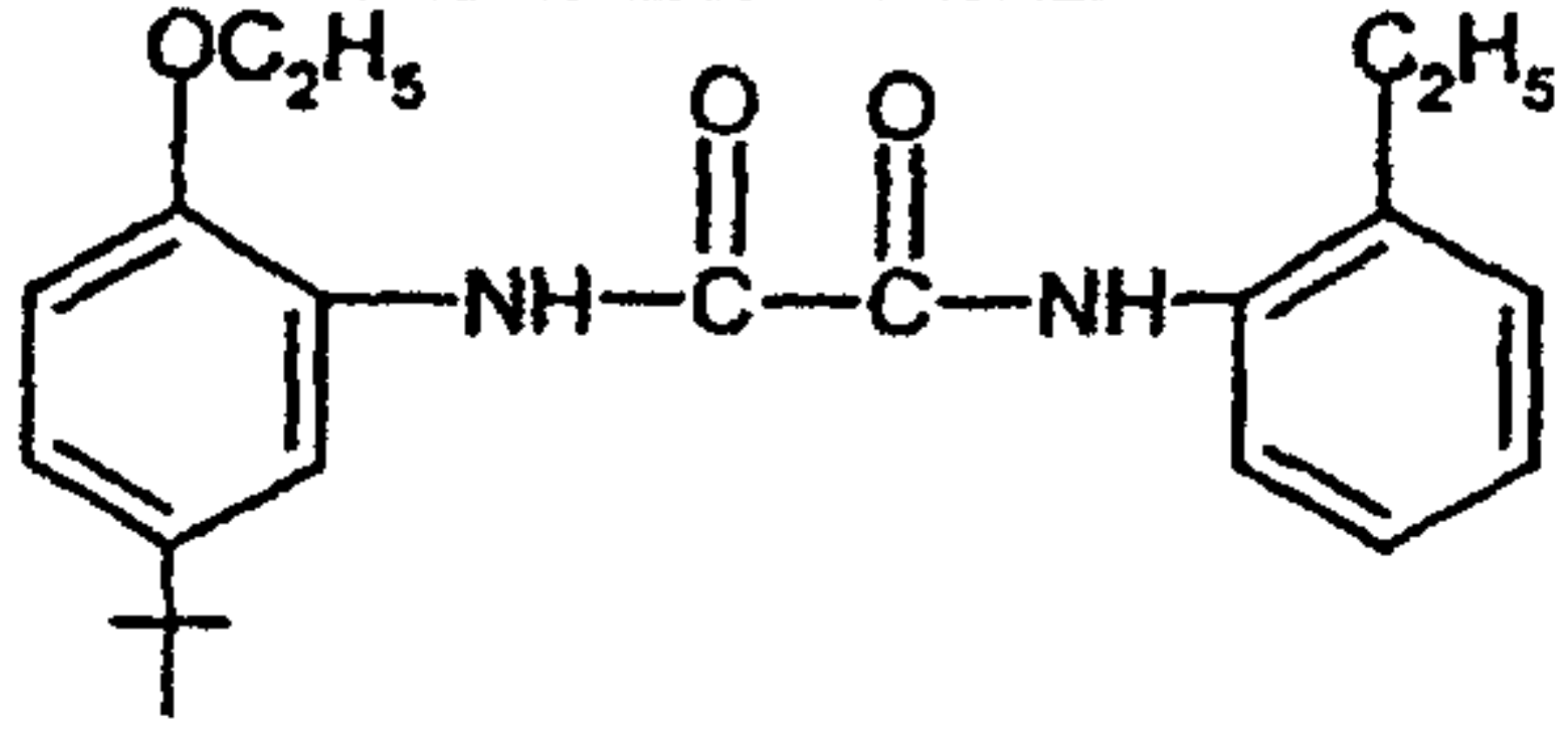
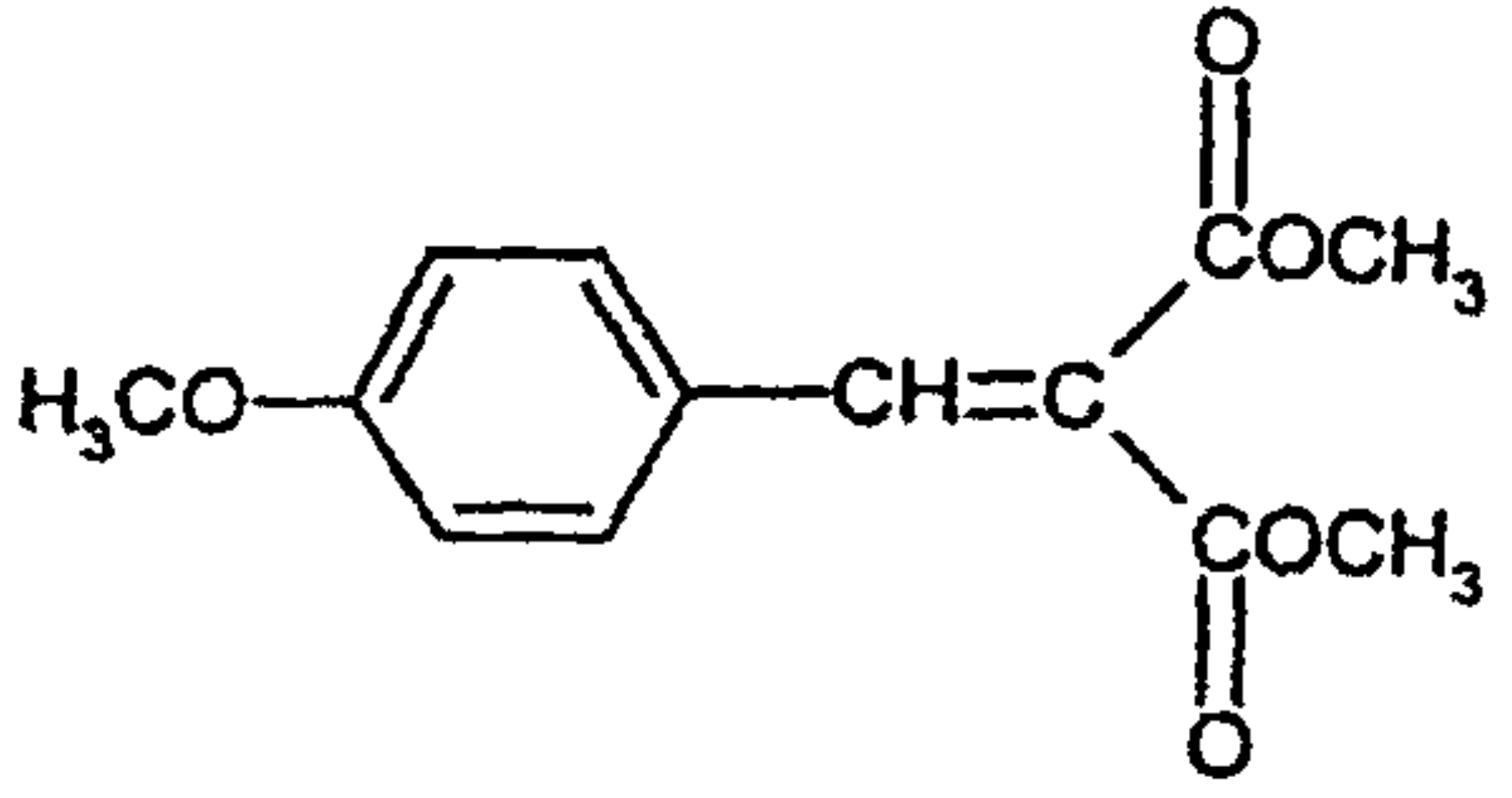
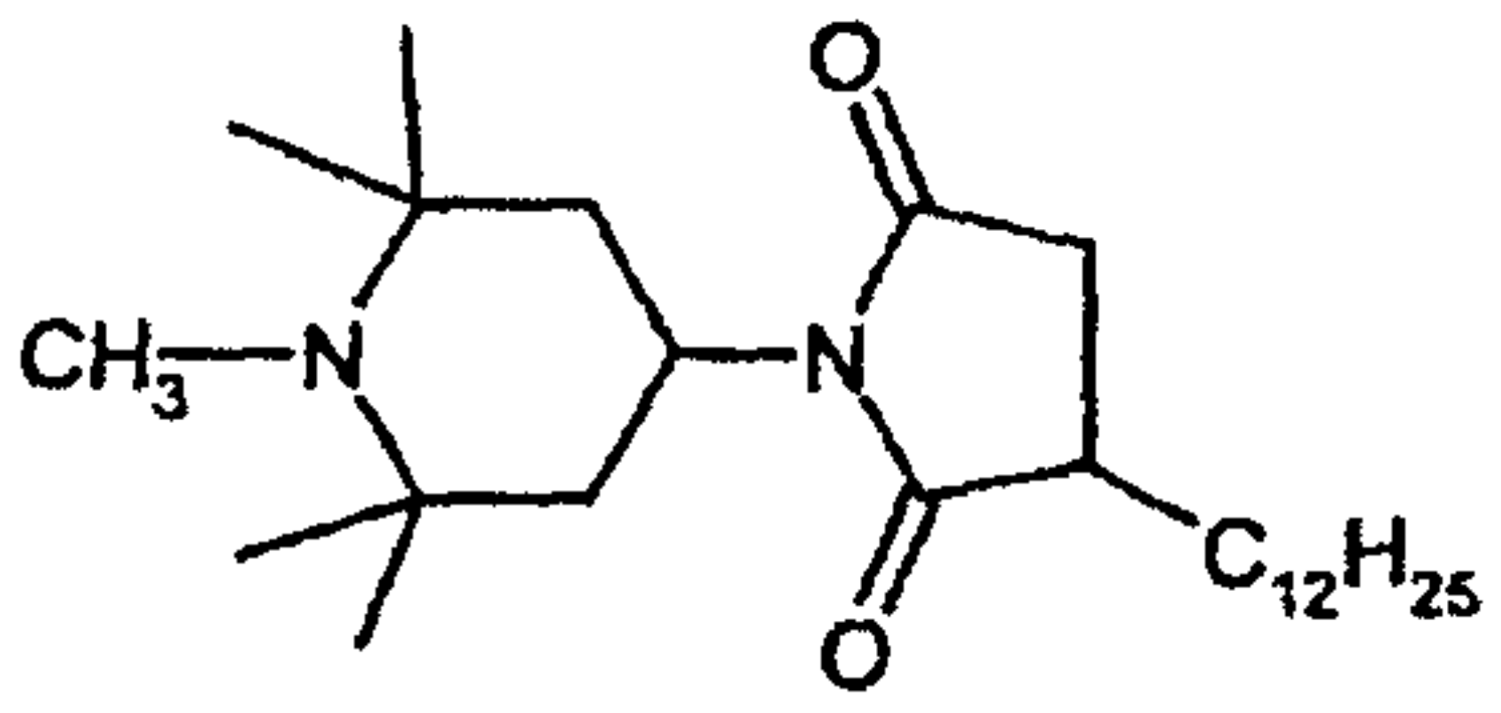
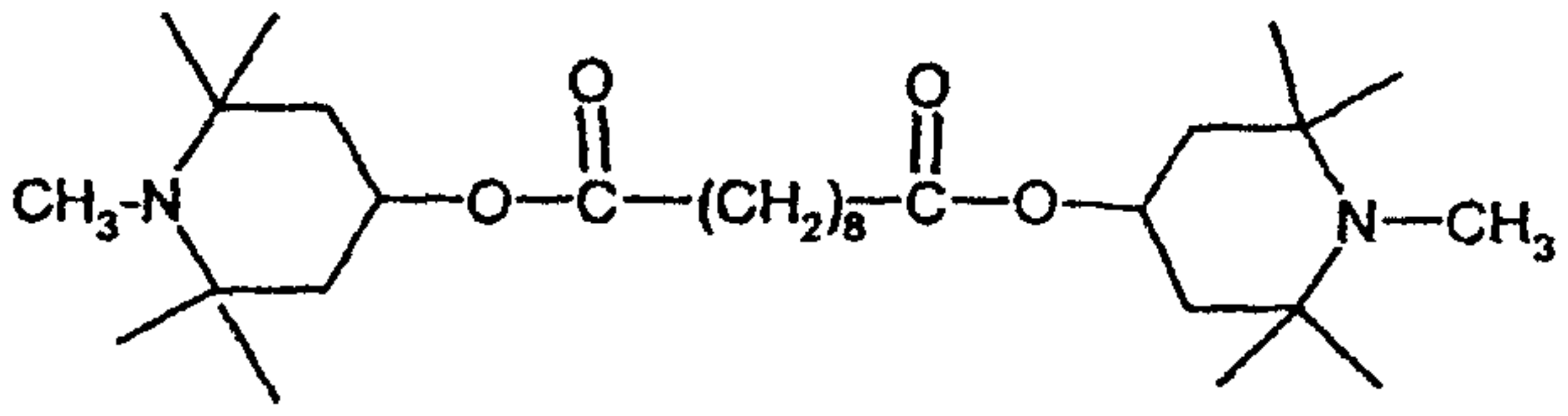
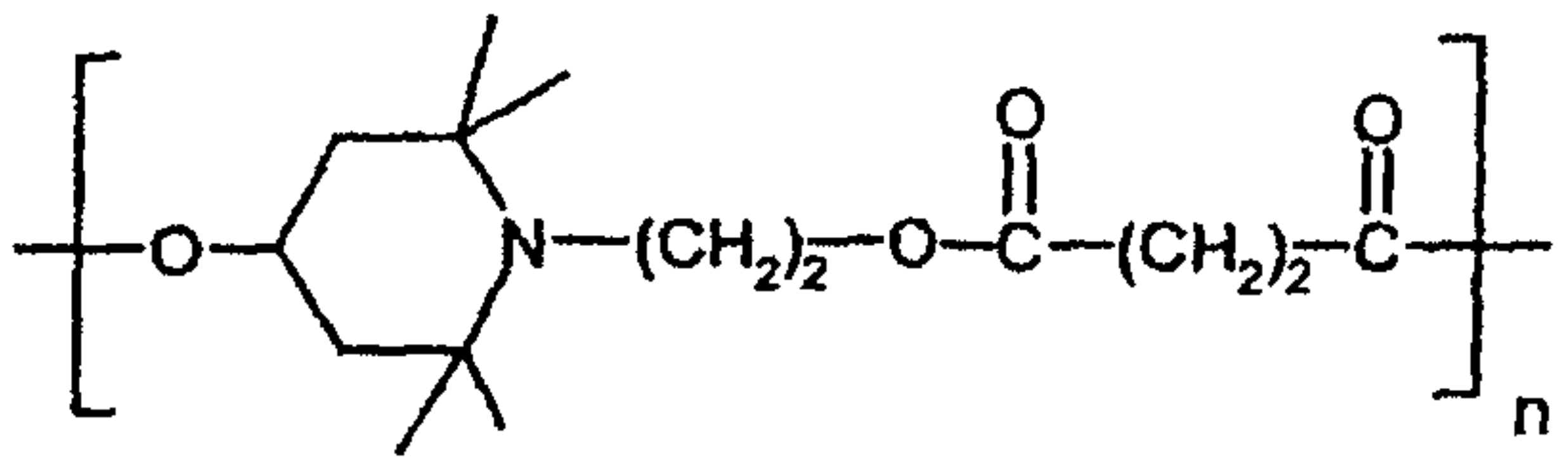
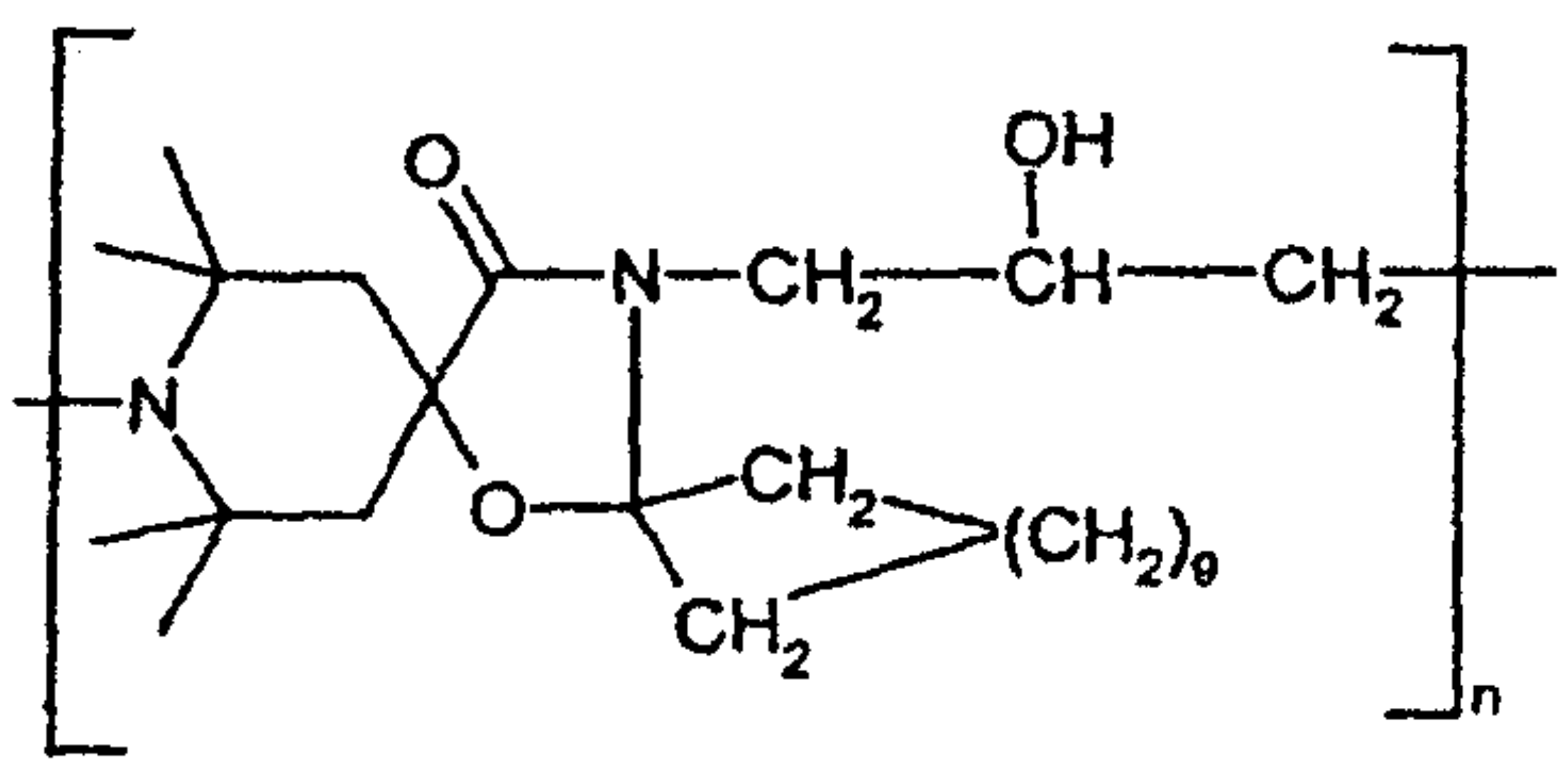
23949-66-8	
35001-52-6	
7443-25-6	
106917-30-0	
41556-26-7	
65447-77-0	
78276-66-1	

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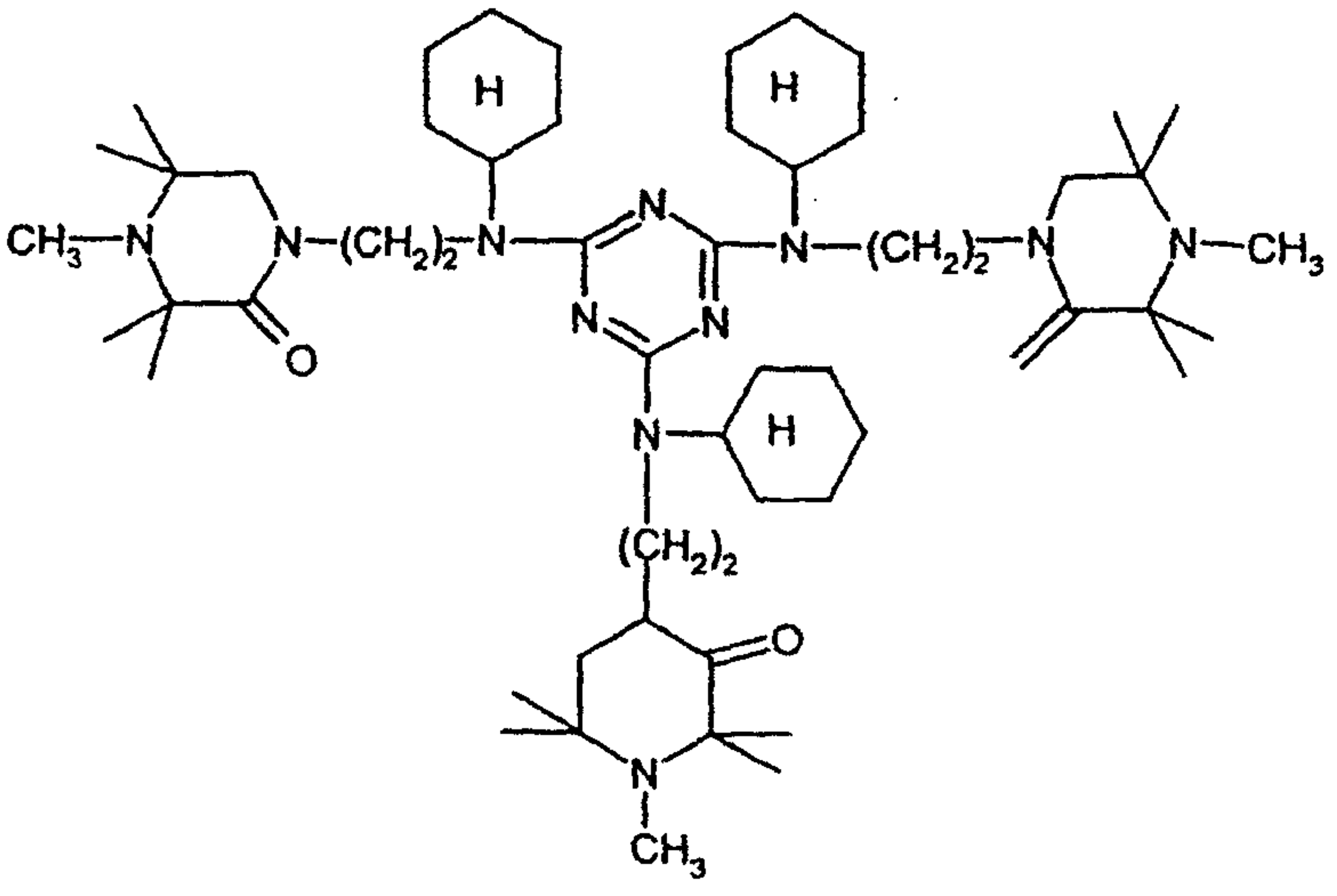
130277-45-1	

The binder compositions according to the invention are obtained by reacting the component A1) with the components A2), A3), A4), A5), a), b) and c) in any desired sequence, optionally with the aid of an organic solvent. The use of all methods, known from the prior art, for the preparation of PU dispersions, such as, for example, the emulsifier shear force process, the acetone process, the prepolymer mixing process, the melt emulsification process, the ketimine process and the solid spontaneous dispersing process or derivatives thereof, is possible for this purpose. A summary of these methods appears in "Methoden der organischen Chemie" [Methods of organic chemistry] (Houben-Weyl, supplementary and subsequent volumes for the 4th edition, Volume E20, H. Bartl and J. Falbe, Stuttgart, New York, Thieme 1987, pages 1617 - 1682).

Preferably, A1) is first reacted with the components A2), A5), a) and b), optionally in the presence of a catalyst. The prepolymer thus prepared is then dissolved in a solvent, optionally in combination with the components b) and/or c), and the components A3) and A4) are then added. The hydrophilized prepolymer thus obtained and dissolved in a solvent is converted into an aqueous dispersion or solution in a further step by adding water. In addition, it is also possible to add further components A3) and A4). The organic solvent used can be removed by distillation after the dispersing.

The binder compositions according to the invention have a solids content of 10 to 70% by weight. Solids contents of 20 to 60% by weight are preferred, particularly preferably 25 to 60% by weight, the proportion of organic solvent, based on the total composition, preferably being less than 15% by weight and particularly preferably less than 5% by weight.

The binder compositions according to the invention are used either alone or in combination with other aqueous binders for the preparation of coating materials. Such aqueous binders can be composed, for example, of polyester polymers, polyacrylate polymers, polybutadiene polymers, polyvinyl acetate polymers, polyepoxide polymers or other polyurethane polymers. The combination with radiation-curable binders, as described, for example, in EP-A-0 753 531, is also possible.

The present invention also relates to a coating material containing the binder compositions according to the invention.

The invention furthermore relates to a process for the preparation of coating materials, characterized in that the binder compositions according to the invention are used.

Coatings based on the compositions according to the invention can be applied to any desired substrates, for example metal, wood, glass, glass fibres, carbon fibres, stone, ceramic minerals, concrete, rigid and flexible plastics of various types, woven and nonwoven textiles, leather, paper, hard fibres, straw and bitumen, which can optionally also be provided with customary primer coats prior to coating. Preferred substrates are glass fibres, carbon fibres, metals, textiles and leather. A particularly preferred substrate comprises glass fibres.

The binder compositions according to the invention can be used as such or in combination with the auxiliaries and additives known from coating technology, such as, for example, nonionic and/or anionic thickeners, fillers, pigments, waxes, handle compositions, dyes, solvents, levelling agents and crosslinking agents for the production of coatings.

It is furthermore possible to add crosslinking agents prior to application. Hydrophilic or hydrophilized polyisocyanate crosslinking agents are preferably suitable for this purpose.

The application of the coating materials can be effected by known methods, for example by brushing, pouring, knife coating, spraying, rolling or immersion. The coating film can be dried at room temperature or elevated temperature, but also by baking at up to 200°C.

The binder compositions according to the invention are storable and shippable and can be processed at any desired later time. Depending on the chosen chemical composition of the polyurethane, coatings having different properties are obtained. Thus, soft tacky coats and thermoplastic and elastomeric products having a wide range of hardnesses up to glass-hard thermosetting plastics can be obtained. Thus, the binder compositions according to the invention can also be used as adhesives, but the use in glass fibre sizes is preferred.

The binder compositions according to the invention can be used in the sizes alone or preferably with other binders, such as, for example, polyacrylate dispersions, polyurethane-polyacrylate hybrid dispersions, polyvinyl ether or polyvinyl ester dispersions, polystyrene or polyacrylonitrile dispersions, also in combination with crosslinking agents, such as blocked polyisocyanates (crosslinking agents) and amino crosslinking resins, such as, for example, melamine resins.

For the preparation of the sizes, the binder compositions according to the invention are used as binder components and may contain further components, such as emulsifiers, further film-forming resins, adhesion promoters, lubricants and auxiliaries, such as wetting agents or antistatic agents. The adhesion promoters, lubricants and auxiliaries, the process for the preparation of the sizes and the process for sizing glass fibres and the subsequent processing of the glass fibres are known and are described, for example, in K.L. Loewenstein, "The Manufacturing Technology of Continuous Glass Fibres", Elsevier Scientific Publishing Corp., Amsterdam, London, New York, 1983.

The present invention also relates to glass fibres sized with a size containing the binder compositions according to the invention.

Both the known glass types used for glass filament manufacture, such as E, A, C and S glass, and the other products known per se from glass fibre manufacturers are suitable for the sized glass fibres. Among said glass types for the production of continuous glass filaments, the E glass fibres, owing to their freedom from alkali, high tensile strength and a high modulus of elasticity, are the most important for reinforcing plastics.

Both thermoplastic and duromeric polymers can be used as matrix polymers.

Examples:

Compounds used:

Diaminosulphonate:
NH_2-CH_2CH_2-NH-CH_2CH_2-SO_3Na (45% strength in water)

Determination of thermal yellowing:

The binder compositions mentioned below are applied to test metal sheets which have been coated with a commercial, white base coat, e.g. from Spies & Hecker, in a wet coat thickness of 120 µm. The test metal sheets are dried for 30 minutes at room temperature and then baked for 30 minutes at 170°C in a drying oven. Thereafter, the colour measurement is carried out by the CIELAB method. The greater the determined positive b* value here, the greater is the resulting yellow discoloration of the coating of the binder composition.

Example 1: Comparative example

PU dispersion of the prior art in the area of glass fibre sizes

Baybond® PU 401 (anionic-nonionic PU dispersion having a solids content of 40% and a mean particle size of 100-300 nm, Bayer AG, Leverkusen, DE)

Example 2: Comparative example

1 377.0 g of polyester PE 170 HN (Bayer AG, Leverkusen, DE, polyesterpolyol, OH number = 66, molecular weight 1 700), 66.8 g of polyether LB 25 (Bayer AG, Leverkusen, DE, monofunctional polyether based on ethylene oxide/propylene oxide and having an average molecular weight of 2 250 (OH number = 25)) and 0.1 g of Desmorapid® Z (Bayer AG, Leverkusen, DE) are heated to 65°C. Thereafter, a mixture of 499.5 g of isophorone diisocyanate and 343.1 g of acetone is added at 65°C in the course of 5 min and stirring is carried out under reflux until a theoretical NCO value has been reached. The prepared prepolymer is dissolved in 1 760.4 g of

acetone at 50°C and then a solution of 47.3 g of adipic acid dihydrazide, 9.0 g of hydrazine hydrate, 21.4 g of isophoronediamine and 419.0 g of water is metered in within 10 min. After the addition of 189.9 g of diaminosulphonate, stirring is continued for 15 min and dispersing is effected by adding 2 628.1 g of water within 20 min. This is followed by the removal of the solvent by distillation in vacuo, and a storage-stable dispersion having a solids content of 40.5% is obtained.

Example 3: Comparative example

1 496.0 g of Polyester PE 170 HN (Bayer AG, Leverkusen, DE, polyesterpolyol, OH number = 66, molecular weight 1 700), 54.0 g of Polyether LB 25 (Bayer AG, Leverkusen, DE, monofunctional polyether based on ethylene oxide/propylene oxide and having an average molecular weight of 2 250 (OH number = 25)) and 0.1 g of Desmorapid® Z (Bayer AG, Leverkusen, DE) are heated to 65°C. Thereafter, a mixture of 444.4 g of isophorone diisocyanate and 352.0 g of acetone is added at 65°C within 5 min and stirring is continued under reflux until a theoretical NCO value has been reached. The prepared prepolymer is dissolved in a solution of 16.0 g of Irganox® 245 (Ciba Spezialitäten GmbH, Lampertheim, DE), 16.0 g of Tinuvin® 770 DF (Ciba Spezialitäten GmbH, Lampertheim, DE) and 1 671.1 g of acetone at 50°C, and then a solution of 9.0 g of hydrazine hydrate, 19.0 g of isophoronediamine and 121.6 g of water is metered in within 10 min. After the addition of 168.8 g of diaminosulphonate, stirring is continued for 15 min and dispersing is effected by adding 2 971.9 g of water within 20 min. This is followed by the removal of the solvent by distillation in vacuo, and a storage-stable dispersion having a solids content of 40.4% is obtained.

Example 4: According to the invention

1 377.0 g of Polyester PE 170 HN (Bayer AG, Leverkusen, DE, polyesterpolyol, OH number = 66, molecular weight 1 700), 60.8 g of Polyether LB 25 (Bayer AG, Leverkusen, DE, monofunctional polyether based on ethylene oxide/propylene oxide and having an average molecular weight of 2 250 (OH number = 25)) and 44.6 g of the abovementioned hydrazine adduct of 1 mol of hydrazine hydrate and 2 mol of

propylene carbonate, having a molecular weight of 236 and of the formula VII, and 0.1 g of Desmorapid® Z (Bayer AG, Leverkusen, DE) are heated to 65°C. Thereafter, a mixture of 499.5 g of isophorone diisocyanate and 349.8 g of acetone is added at 65°C within 5 min and stirring is carried out under reflux until a theoretical NCO value has been reached. The prepared prepolymer is dissolved by adding a solution of 1 880.0 g of acetone, 11.2 g of Irganox® 245 (Ciba Spezialitäten GmbH, Lampertheim, DE) and 11.2 g of Tinuvin® 770 DF (Ciba Spezialitäten GmbH, Lampertheim, DE) at 50°C, and a solution of 7.8 g of adipic acid dihydrazide, 9.0 g of hydrazine hydrate, 21.4 g of isophoronediamine and 136.6 g of water is then metered in within 10 min. After the addition of 189.9 g of diaminosulphonate, stirring is continued for 15 min and dispersing is effected by adding 2 942.7 g of water within 20 min. This is followed by the removal of the solvent by distillation in vacuo, and a storage-stable dispersion having a solids content of 40.8% is obtained.

Table 3:

	Example 1 Baybond® PU 401 (Comparative example, prior art)	**Example 2** (Comparative example)	**Example 3** (Comparative example)	**Example 4** (according to the invention)
Solids content [%]	40%	40.5	40.4	40.8
Mean particle size [nm]	100-300 nm	161.0	165.5	162.7
Compound of the formula VII	-	-	-	X
Tinuvin 770 DF	-	-	X	X
Adipic acid dihydrazide	-	X	-	X
CIE/LAB b* values	1.3	0.5	0.9	0.0

The results shown in Table 3 demonstrate that the PU dispersion of Example 4, according to the invention, exhibits substantially less yellowing compared with PU dispersions of the prior art (Example 1) and conventionally stabilized PU dispersions (Examples 2 and 3).

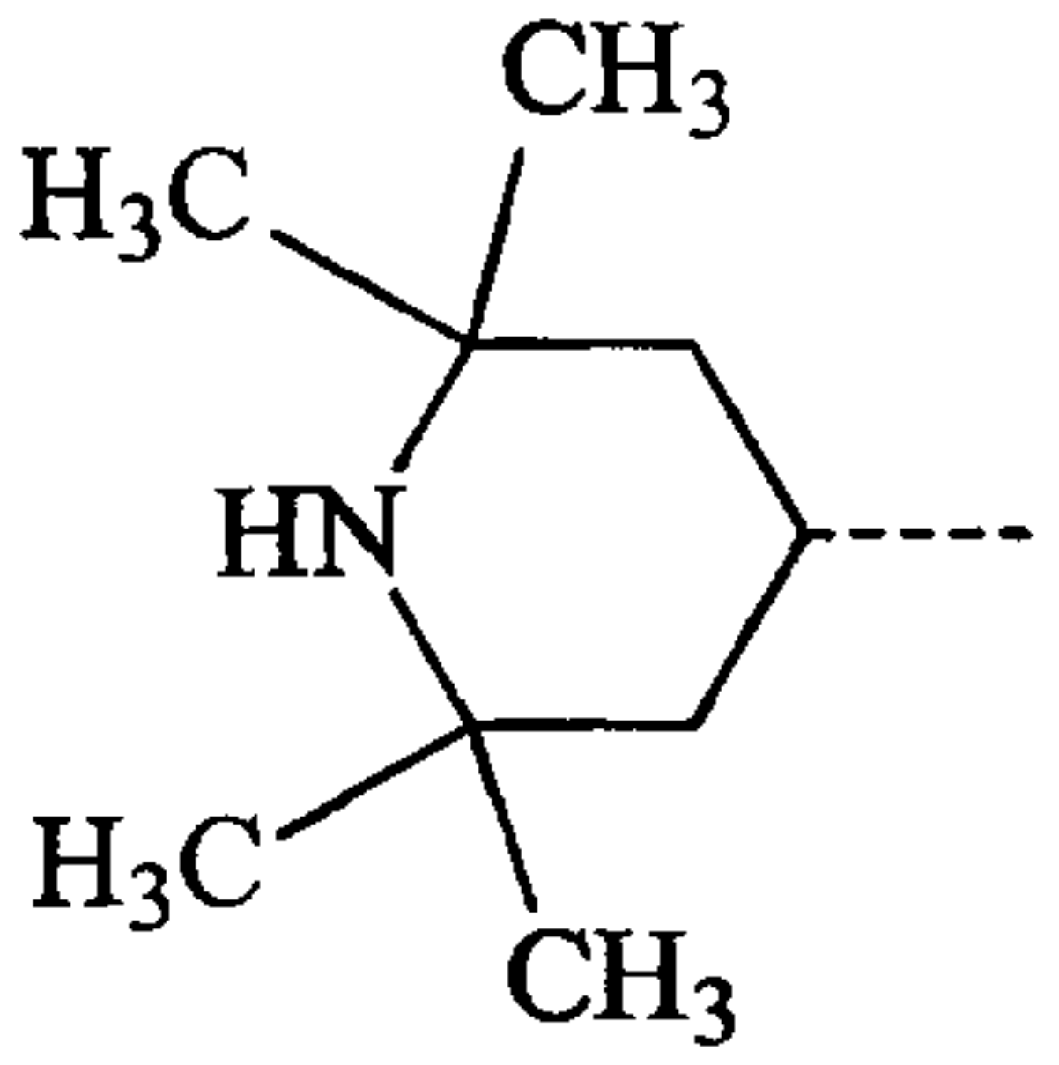
CLAIMS:

1. A binder composition, containing:

(A) at least one aqueous PU dispersion; and

(B) at least one stabilizer or stabilizer mixture, containing:

(a) at least one amine having a structural unit of the formula (I):



(I)

which has no hydrazide groups,

(b) at least one compound having a structural unit of the formula (II):

-CO-NH-NH- (II)

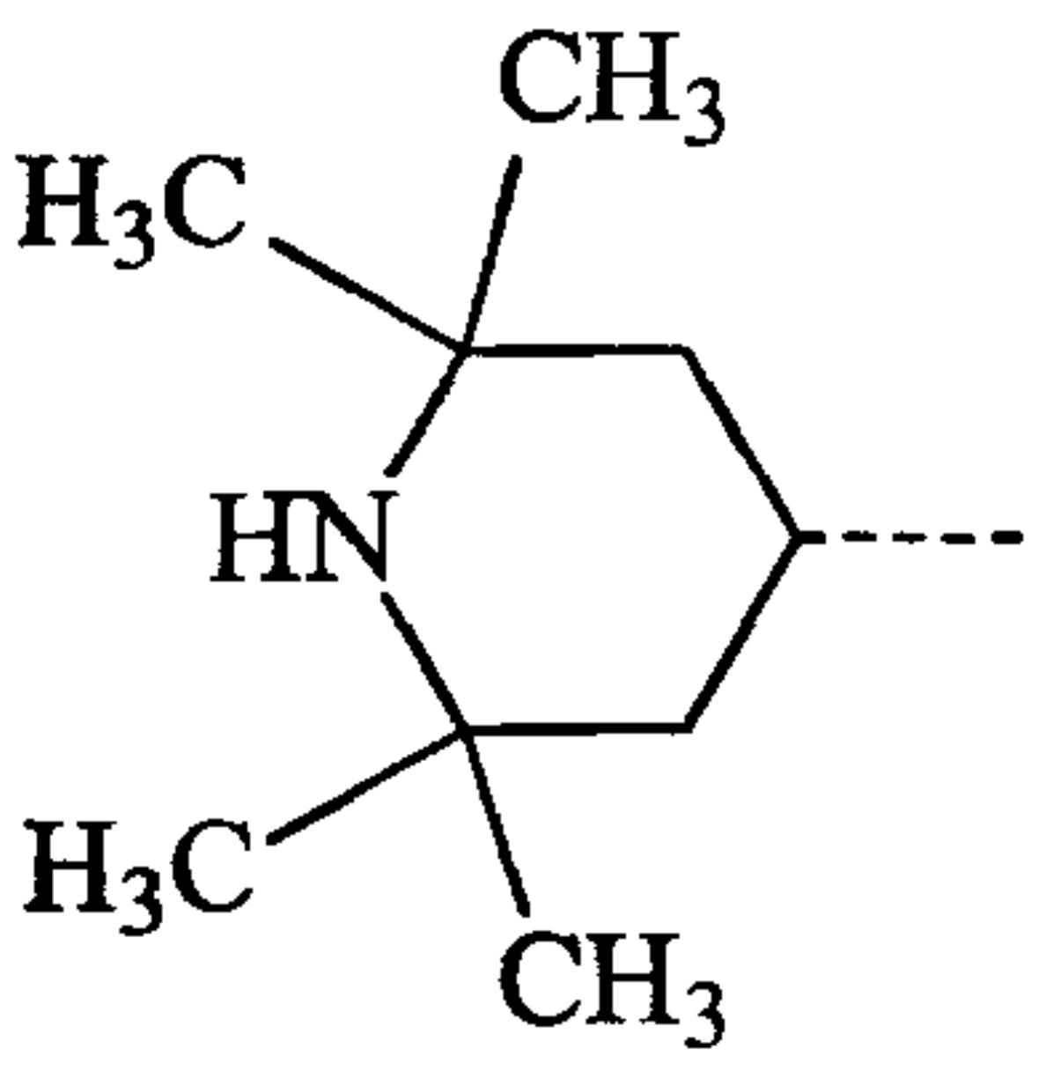
and

(c) optionally, a stabilizing component differing from (a) and (b).

2. A binder composition, containing:

(A) at least one aqueous PU dispersion containing structural units or at least one stabilizer or stabilizer mixture (B) based on:

(a) at least one amine having a structural unit of the formula (I):



(I)

which has no hydrazide groups,

(b) at least one compound having a structural unit of the formula (II):

-CO-NH-NH- (II)

and

(c) optionally, a stabilizer component differing from (a) and (b).

3. The binder composition according to claim 1 or 2, containing, based on total solids content, 78.0 to 99.8% by weight of component (A) and 0.2 to 22.0% by weight of component (B), the sum of the components being 100%.

4. The binder composition according to claim 1 or 2, containing, based on total solids content, (a) 0.1 to 11.0% by weight of at least one amine having the structural unit of the formula (I), (b) 0.1 to 11.0% by weight of a hydrazide having the structural unit of the formula (II) and (c) 0 to 5.0% by weight of another stabilizer differing from (a) and (b).

5. The binder composition according to any one of claims 1 to 4, wherein the aqueous PU dispersion (A) is composed of the components:

(A1) a polyisocyanate;

(A2) a polymeric polyol having an average molecular weight of 400 to 6 000;

(A3) optionally, a mono- or polyalcohol, or a mono- or polyamine;

and at least one compound which is

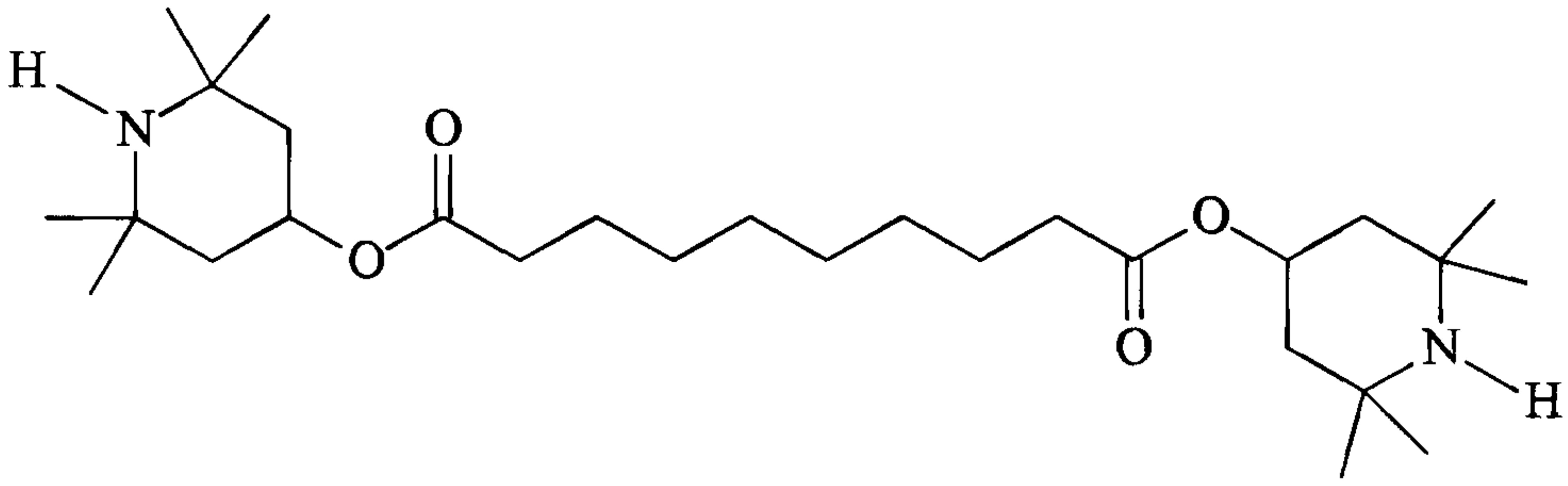
(A4) a compound which has at least one ionic or potentially ionic group; or

(A5) a nonionically hydrophilized compound.

6. The binder composition according to claim 5, wherein the aqueous PU dispersion (A) contains 7 to 45% by weight of (A1), 50 to 91% by weight of (A2), 0 to 30% by weight of (A3), 0 to 15% by weight of (A5), 0 to 12% by

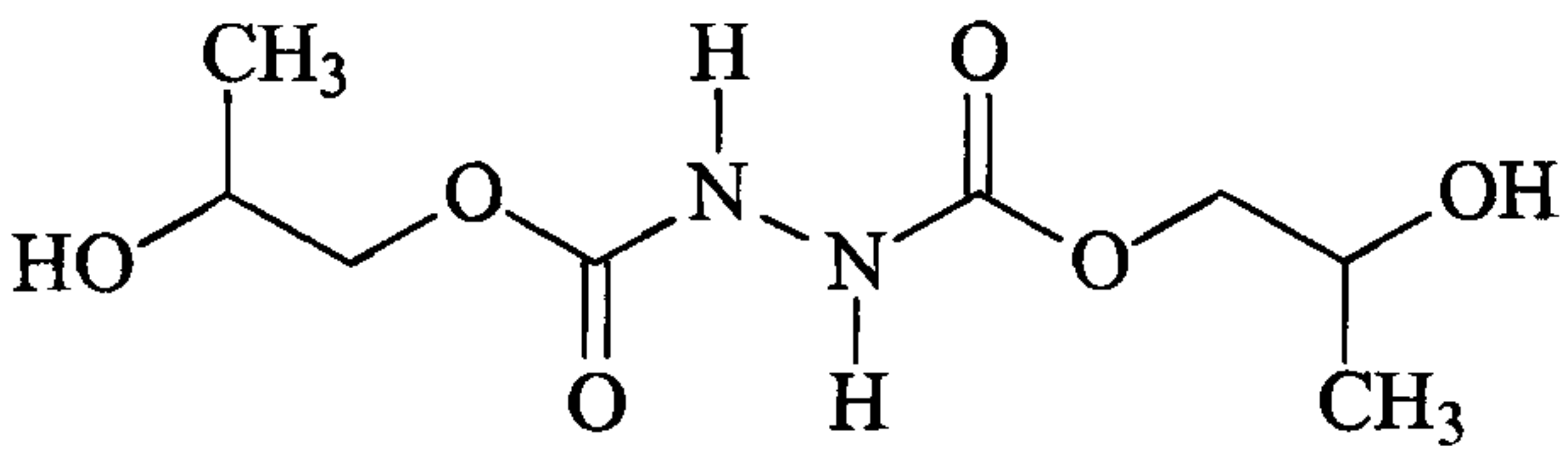
weight of (A4), wherein the sum of the components (A1) to (A5) is 100% by weight and the sum of the components (A4) and (A5) is not equal to 0.

7. The binder composition according to any one of claims 1 to 6, wherein the amine (a) is a compound of the formula (VI):



(IV)

8. The binder composition according to any one of claims 1 to 7, wherein the compound (b) is a compound of the formula (VII):



(VII)

9. A process for the preparation of a binding composition according to claim 5, wherein a prepolymer is first prepared by reacting the component (A1) with the components (A2), (A5), (a) and (b), optionally in the presence of a catalyst, and the prepolymer is then dissolved in a solvent, optionally in combination with the components (b), (c) or a combination thereof, and then the components (A3) and (A4) are added and, in a further step, the prepolymer thus obtained is converted into an aqueous dispersion or solution by adding water.

10. Use of the binder composition according to any one of claims 1 to 8, in a glass fibre size.

11. Use of the binder composition according to any one of claims 1 to 8, in an adhesive.

12. A coating material containing the binder composition according to any one of claims 1 to 8.

13. A glass fibre sized with a size containing the binder composition according to any one of claims 1 to 8.

FETHERSTONHAUGH & CO.
OTTAWA, CANADA

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