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(54) **Titre : FIXATION POLYMER-METAL ET COMPOSES ET COMPOSITIONS UTILES POUR CELLE-CI**  
(54) **Title: POLYMER TO METAL BONDING AND COMPOUNDS AND COMPOSITIONS USEFUL THEREFOR**

(57) **Abrégé/Abstract:**

A compound comprising at least one alkoxy silane moiety; and at least one moiety selected from a nitrosobenzene or a nitrosobenzene precursor and combinations thereof are provided and used in polymer to metal, in particular rubber to metal bonding. The nitrosobenzene precursor may be at least one of a quinone dioxime or a quinone oxime. The invention also provides for a compound comprising at least one alkoxy silane moiety; and at least one moiety selected from an aromatic nitroso or an aromatic nitroso precursor and combinations thereof.

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(54) **Title:** POLYMER TO METAL BONDING AND COMPOUNDS AND COMPOSITIONS USEFUL THEREFOR(57) **Abstract:** A compound comprising at least one alkoxy silane moiety; and at least one moiety selected from a nitrosobenzene or a nitrosobenzene precursor and combinations thereof are provided and used in polymer to metal, in particular rubber to metal bonding. The nitrosobenzene precursor may be at least one of a quinone dioxime or a quinone oxime. The invention also provides for a compound comprising at least one alkoxy silane moiety; and at least one moiety selected from an aromatic nitroso or an aromatic nitroso precursor and combinations thereof.

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## Polymer to Metal Bonding and Compounds and Compositions Useful Therefor

### **BACKGROUND**

#### **Field**

[0001] Adhesive compositions suitable for use in polymer-to-metal, for example elastomer-to-metal such as rubber-to-metal, bonding applications are provided. One aspect provides compounds suitable for use in such adhesive composition rubber to metal bonding applications.

#### **Brief Description of Related Technology**

[0002] Polymer to metal and in particular rubber to metal bonding has been practised for many years. There are many applications for formulations which achieve polymer or rubber to metal bonding. Rubber to metal bonding is widely used to bond different metals to a natural or synthetic rubber. Polymer to metal bonding is carried out for many reasons.

[0003] One aspect of rubber to metal bonding is to combine the structural strength of the metal with the elastomeric properties of the rubber.

[0004] Accordingly, metal and polymers such as rubber are often bonded to each other for impact absorption applications, such as in bearings, wheels, shock absorbers, moving arms, *etc.* Such components can be utilised on a very small scale, for example in PC components or on a very large scale for example in constructions such as bridges and buildings. Noise reduction may also be achieved by utilising metal to rubber bonding. It is accepted that tremendous forces can be experienced by any component that comprises metal and rubber bonded together. Accordingly, it is desirable to provide metal to rubber bonding, which can withstand significant forces, such as compressive or extensive pressures including shocks without having the metal or the rubber separate from each other. There are many other rubber to metal bonding applications, including tyre production where internal wire reinforcements for the tyre are bonded to the rubber of the tyre.

[0005] Generally, an adhesive formulation is provided to bond a selected rubber to a selected metal substrate.

[0006] Traditional rubber-to-metal bonding technology incorporates a two-step system, where in a first step a primer is applied and thereafter in a second step an adhesive is applied. The primer ordinarily consists of solutions or suspensions of chlorinated rubber and phenolic resins containing reactive groups, and also pigments such as titanium dioxide, zinc oxide, carbon black, *etc.* The primer is generally applied as a thin layer onto a treated (cleaned) surface of a metallic component such as treated steel component for example a component that has been grit blasted or chemically treated.

[0007] The adhesive ordinarily consists of a large range of rubber materials and cross-linkers. These include, but are not restricted to, chlorinated and bromochlorinated rubbers, aromatic nitrosobenzene compounds and bismaleimide as cross-linkers, xylene, perchloroethylene and ethylbenzene as solvents, and also some lead or zinc salts. The adhesive layer is generally the link between the primed metal and the rubber.

[0008] Common cross-linkers that have been employed in rubber-to-metal bonding technology are aromatic nitroso compounds, such as *p*-dinitrosobenzene.

[0009] In the many fields where rubber to metal bonding is employed there are numerous opportunities to address several types of problems, including bond strength and durability, sample preparation and ease of application of the adhesive, single coat versus two-coat systems, reduced toxicity and improved properties for the environment, amongst others.

[0010] Many formulations for rubber to metal bonding exist. For example silanes have been used as corrosion inhibitors and as rubber-to-metal bonding adhesion promoters. Reducing VOCs (volatile organic compounds) and reducing the costs, such as those associated with cobalt salts, which are used as adhesion promoters in certain systems is desirable for example as set out in the following U.S. Patent Application Publication Nos. U.S. 2007/0056469A1 and U.S. 2005/0079364A1, and U.S. Patent Nos. 6756079B2 and U.S. 6409874. Specific silanes noted are *bis*(trimethoxypropyl)amine and *bis*(triethoxypropyl)tetrasulfide, generally in use together in a ratio of 1:3 respectively, in an ethanol/water solution. It is noteworthy that the silanes are thus hydrolysed, either separately or together, prior to application to the metal.

[0011] International Patent Publication No. WO2004/000851 to Qinetiq Ltd., describes a process for silane hydrolysis with a good degree of control. The process is

carried out in solution in the presence of water and a catalyst. International (PCT) patent publication No. WO2004/078867 to Lord Corporation describes a single coat solvent-based adhesive designed to bond thermoplastic elastomers containing an alkoxy silane/urethane adduct and a chlorinated polymer. Methods of synthesis and formulation are described within this patent document. U.S. Patent No. 4,031,120 to Lord Corporation describes a composition comprising an isocyanate functional organosilane, in combination with a polyisocyanate and an aromatic nitroso compound. The resulting system is described as a one-coat adhesive for bonding a variety of elastomeric materials to metals and other substrates.

[0012] Generally, it is desirable that bonding is achieved during a vulcanisation step like compression moulding, transfer moulding, injection moulding and autoclave heating, for example with steam or hot air. For example, semi-solid rubber can be injected into a mould. The semi-solid rubber is then cross-linked into a fully cured rubber and the bond with the substrate is formed at the same time.

[0013] Certain requirements of the curing system are desirable. This includes, ease of processing, stability (for example avoiding sedimentation), ease of application, fast drying (to allow handling without fouling), good wetting properties, and good curing strengths. Curing should be achieved independently of the type of elastomer (rubber) employed and also independently of the type of substrate. It will be appreciated that some rubbers are blended materials and accordingly it is desirable that good curing is achieved with such blended materials. Suitably consistent curing is achieved under various process parameters. Durability is also desirable. For example, the rubber/metal joint should be durable under relatively high mechanical stress for example under high pressure and even if exposed to an aggressive atmosphere, for example a hot liquid such as oil.

[0014] Notwithstanding the state of the technology it would be desirable to provide a compound and composition to bond polymeric substrates to metal substrates that remedies some or all of the known deficiencies and/or provides alternatives to the existing technologies so that consumers have more possibilities from which to choose.

**Summary**

[0015] Compounds suitable for use in rubber to metal bonding are provided.

[0016] In a first aspect a compound is provided comprising:

a) at least one alkoxy silane moiety; and

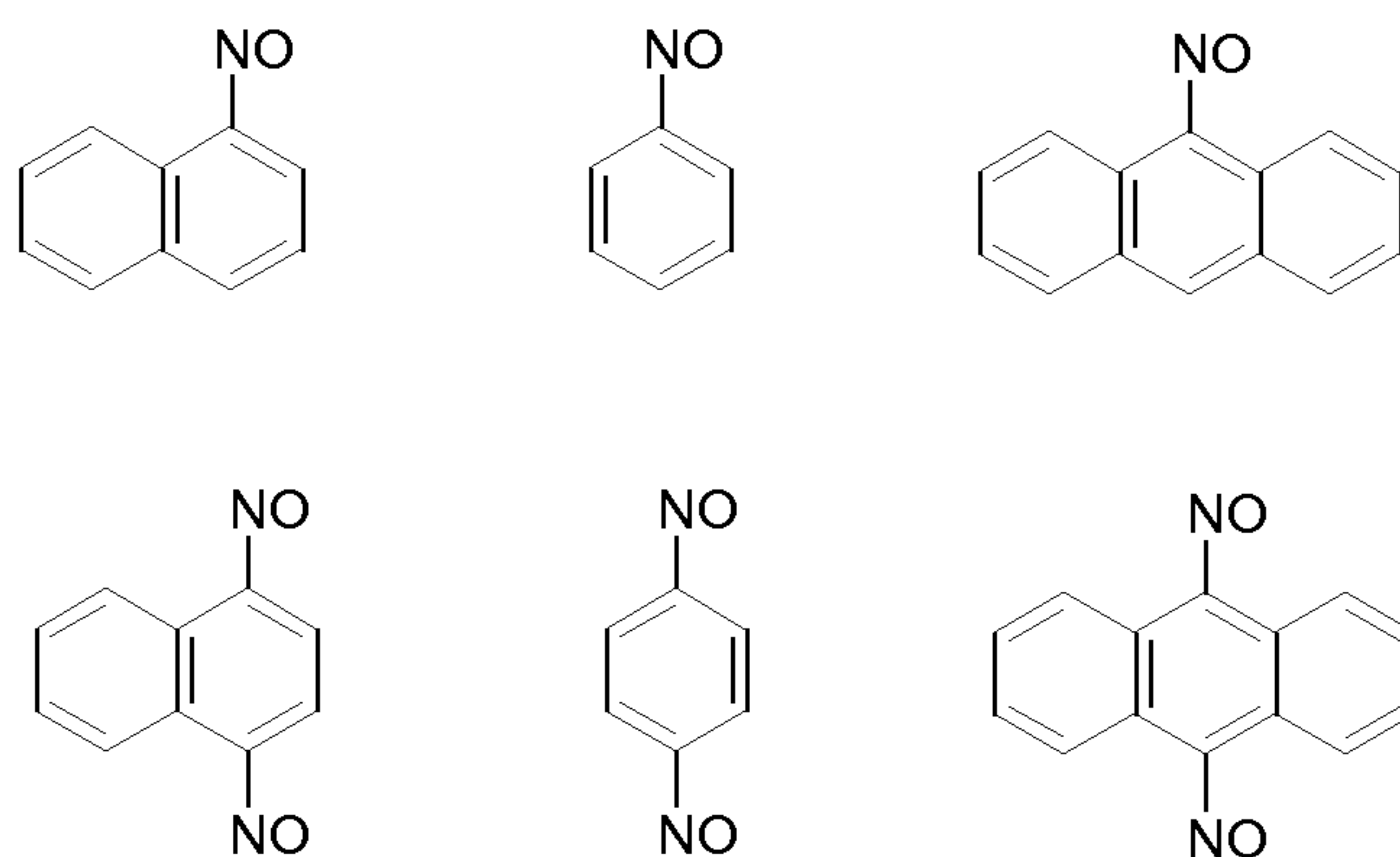
b) at least one moiety selected from an aromatic nitroso or an aromatic nitroso precursor and combinations thereof.

[0017] The compound may comprise:

a) at least one alkoxy silane moiety; and

b) at least one moiety selected from a nitrosobenzene or a nitrosobenzene precursor and combinations thereof.

[0018] Within the context of this specification the term aromatic nitroso moiety refers to an aromatic moiety having at least one nitroso group. Similarly, the term aromatic nitroso precursor moiety refers to any compound that is capable of being transformed into an aromatic nitroso moiety with at least one nitroso group. The term aromatic comprises both fused and non-fused aromatic rings. For example, a non-limiting selection of fused and non-fused aromatic nitroso moieties embraced by the present invention are detailed below:



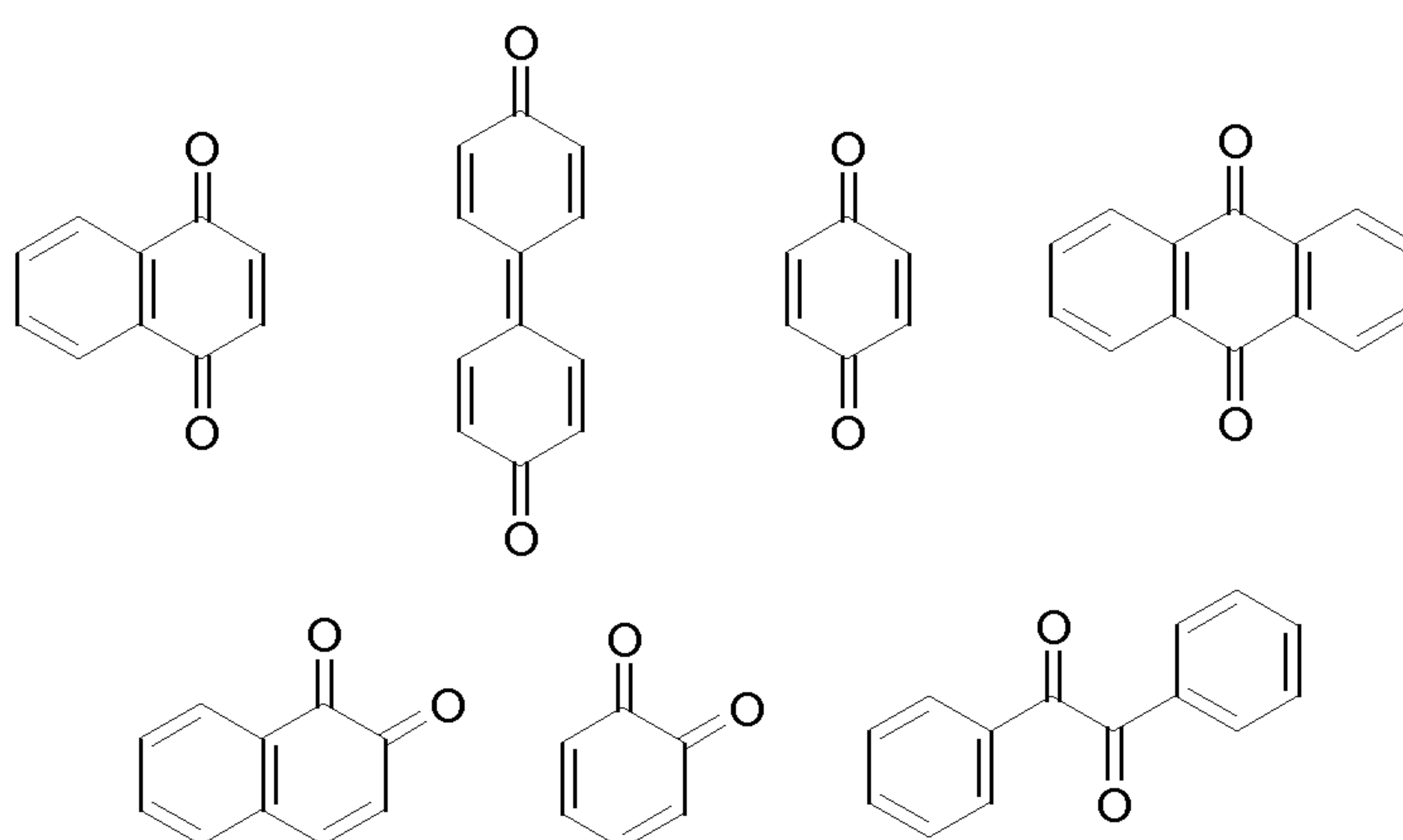
[0019] As will be appreciated by a person skilled in the art, the nitroso structures disclosed above may optionally be substituted one or more times, for example with at least one of C<sub>1</sub>-C<sub>20</sub> alkyl, C<sub>1</sub>-C<sub>20</sub> cycloalkyl, C<sub>1</sub>-C<sub>20</sub> alkoxy, C<sub>6</sub>-C<sub>20</sub> aralkyl, C<sub>6</sub>-C<sub>20</sub> alkaryl, C<sub>6</sub>-C<sub>20</sub> arylamine, C<sub>6</sub>-C<sub>20</sub> arylnitroso, cyano, amino, hydroxy, halogen and combinations thereof. Such substitutions are possible provided there is no interference with effective bonding or curing of the compositions.

[0020] Such compounds assist in the formation of rubber to metal bonds. They can be easily applied at the interface between the rubber and the metal and assist in developing strong and durable bonds during the curing process.

[0021] The so-described compounds and formulations may result in a number of advantages. For example, a one-part adhesive system may be formulated. Such systems are readily applied to substrates in a single step using convenient and conventional techniques, for example spraying or dipping. Compounds and formulations as so provided may have reduced toxicity as compared to conventional dinitrosobenzene formulations. Compounds and formulations as so provided can also achieve excellent bond strengths. For example, in rubber to metal bonding tests to determine the bond strength of the compositions of the present invention 85-100% rubber failure was observable. In a number of examples 100% rubber failure was observed. In addition, cured compositions of the present invention exhibit hot water and solvent resistance. Rubber failure relates to failure of the rubber before the bond fails. That is, the bond is stronger than the rubber substrate.

[0022] In contrast to conventional systems the adhesive systems of the present invention can be applied to the unvulcanised rubber, (as distinct from the metal), prior to vulcanisation and bond formation, and upon subsequent vulcanization a bond results. This means that the adhesive system may be applied to either the rubber or the metal substrate. Conventional systems do not form a bond if applied in this manner.

[0023] The aromatic nitroso precursor moiety may comprise any aromatic oxime, aromatic dioxime and combinations thereof. For example, the aromatic nitroso precursor moiety may be the mono- or dioxime of a compound selected from the group consisting of:

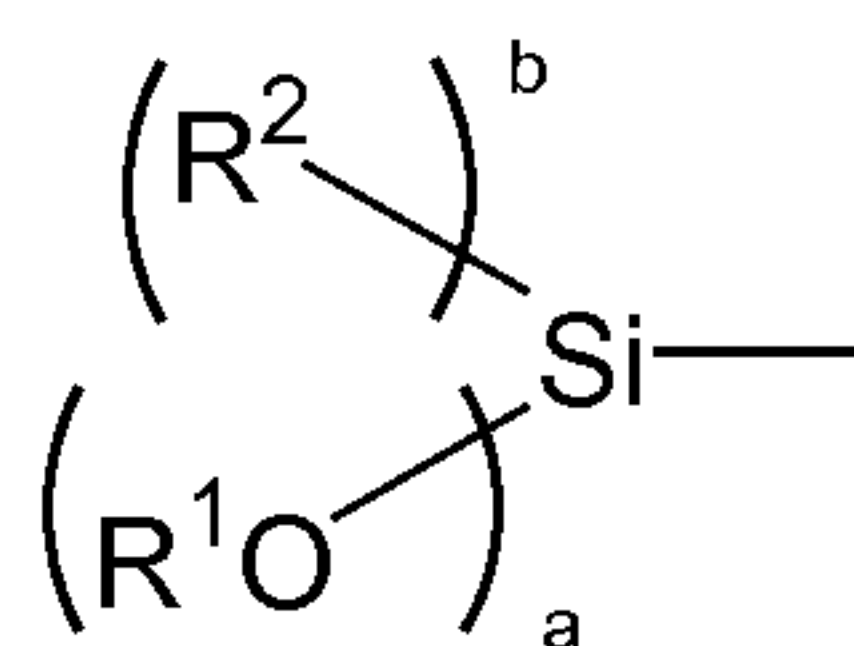


[0024] As will be appreciated by a person skilled in the art, the diketone structures disclosed above may optionally be substituted one or more times, for example with at least one of C<sub>1</sub>-C<sub>20</sub> alkyl, C<sub>1</sub>-C<sub>20</sub> cycloalkyl, C<sub>1</sub>-C<sub>20</sub> alkoxy, C<sub>6</sub>-C<sub>20</sub> aralkyl, C<sub>6</sub>-C<sub>20</sub> alkaryl, C<sub>6</sub>-C<sub>20</sub> arylamine, C<sub>6</sub>-C<sub>20</sub> arylnitroso, cyano, amino, hydroxy, halogen and combinations thereof. Such substitutions are possible provided there is no interference with effective bonding or curing of the compositions, for example, with the generation of an aromatic nitroso compound *in-situ*.

[0025] The aromatic nitroso moiety of the compound of the present invention may comprise a nitrosobenzene moiety. The nitrosobenzene moiety may be a mononitrosobenzene, a dinitrosobenzene, or combinations thereof. Similarly, the aromatic nitroso precursor moiety of the composition of the present invention may comprise a nitrosobenzene moiety precursor. The nitrosobenzene precursor may be a mononitrosobenzene precursor, a dinitrosobenzene precursor, or combinations thereof. It will be appreciated that the nitrosobenzene precursor may form a nitrosobenzene structure *in-situ*. The nitrosobenzene precursor may be at least one of a quinone dioxime or a quinone oxime. It has been found that such structures assist in the formation of desirable bonds.

[0026] As will be appreciated by a person skilled in the art, references to nitrosobenzene and nitrosobenzene precursor moieties include nitrosobenzene and nitrosobenzene precursor moieties that may optionally be substituted one or more times with at least one of C<sub>1</sub>-C<sub>20</sub> alkyl, C<sub>1</sub>-C<sub>20</sub> cycloalkyl, C<sub>1</sub>-C<sub>20</sub> alkoxy, C<sub>6</sub>-C<sub>20</sub> aralkyl, C<sub>6</sub>-C<sub>20</sub> alkaryl, C<sub>6</sub>-C<sub>20</sub> arylamine, C<sub>6</sub>-C<sub>20</sub> arylnitroso, cyano, amino, hydroxy, halogen and combinations thereof. Such substitutions are possible provided there is no interference with effective bonding or curing of the compositions. For example, provided there is no interference with the generation of a nitrosobenzene moiety *in-situ*.

[0027] The silane moiety may be of the structure:



where 'a' can be 1-3 and 'b' can be 0-2, but if a = 3, b = 0; or if a = 2, b = 1; so that at least one alkoxy group is present;

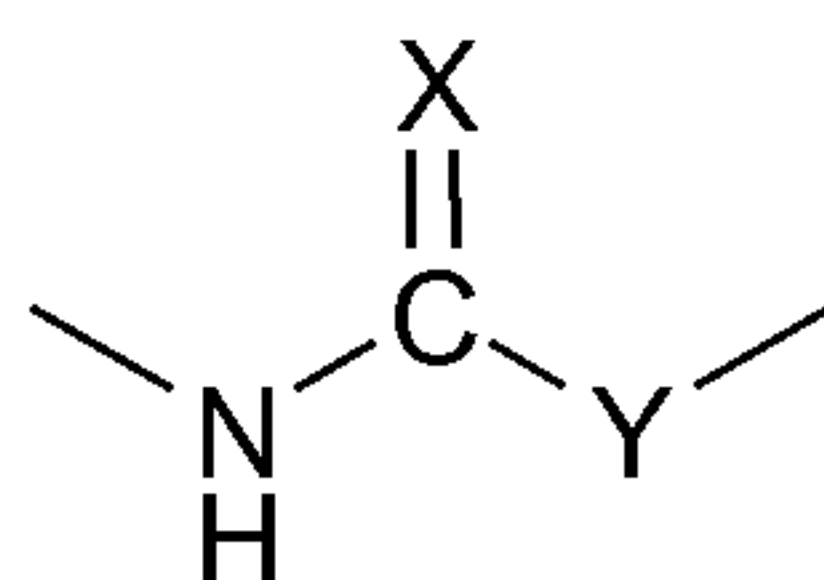
$R^1$  can be selected from the group consisting of H,  $C_1$ - $C_{24}$  alkyl,  $C_3$ - $C_{24}$  acyl, preferably from  $C_1$ - $C_4$  alkyl;

wherein when  $a \geq 1$  at least one  $R^1$  is not hydrogen; and

$R^2$  can be selected from  $C_1$ - $C_{24}$  alkyl and  $C_3$ - $C_{24}$  acyl, preferably from  $C_1$ - $C_4$  alkyl.

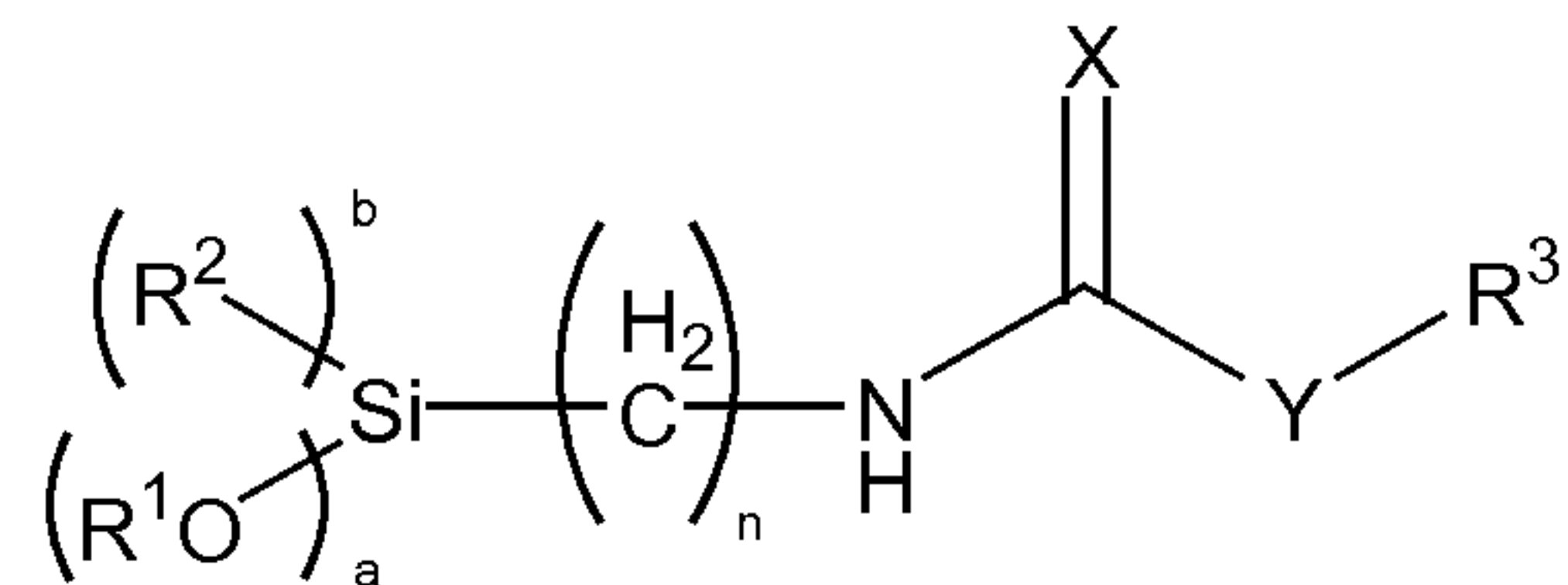
[0028] In one embodiment,  $a$  is 3 and  $R^1$  is  $C_1$ - $C_{24}$  alkyl.  $R^1$  may be  $C_1$ - $C_4$  alkyl and  $a$  may be 3.

[0029] The compounds may be reaction products derived from an isocyanate or isothiocyanate and an active hydrogen compound, such as  $-NH_x$  (where  $x = 1$  or  $2$ ),  $-SH$ , or  $-OH$ . In this manner the so-described compounds should contain at least one linkage described by:



where X can be S or O, and Y includes  $-NH_x$  (where  $x = 1$  or  $2$ ),  $-S$ , or  $-O$ .

[0030] The general structure for these compounds is shown below:



where 'a' can be 1-3 and 'b' can be 0-2; but if  $a = 3$ ,  $b = 0$ ; or if  $a = 2$ ,  $b = 1$ ; so that at least one alkoxy group is present;

$R^1$  can be selected from the group consisting of H,  $C_1$ - $C_{24}$  alkyl,  $C_3$ - $C_{24}$  acyl, preferably from  $C_1$ - $C_4$  alkyl and wherein when  $a \geq 1$  at least one  $R^1$  is not hydrogen; and

$R^2$  can be selected from  $C_1$ - $C_{24}$  alkyl and  $C_3$ - $C_{24}$  acyl, preferably from  $C_1$ - $C_4$  alkyl;  $n$  can be 1-5;

X can be O or S;

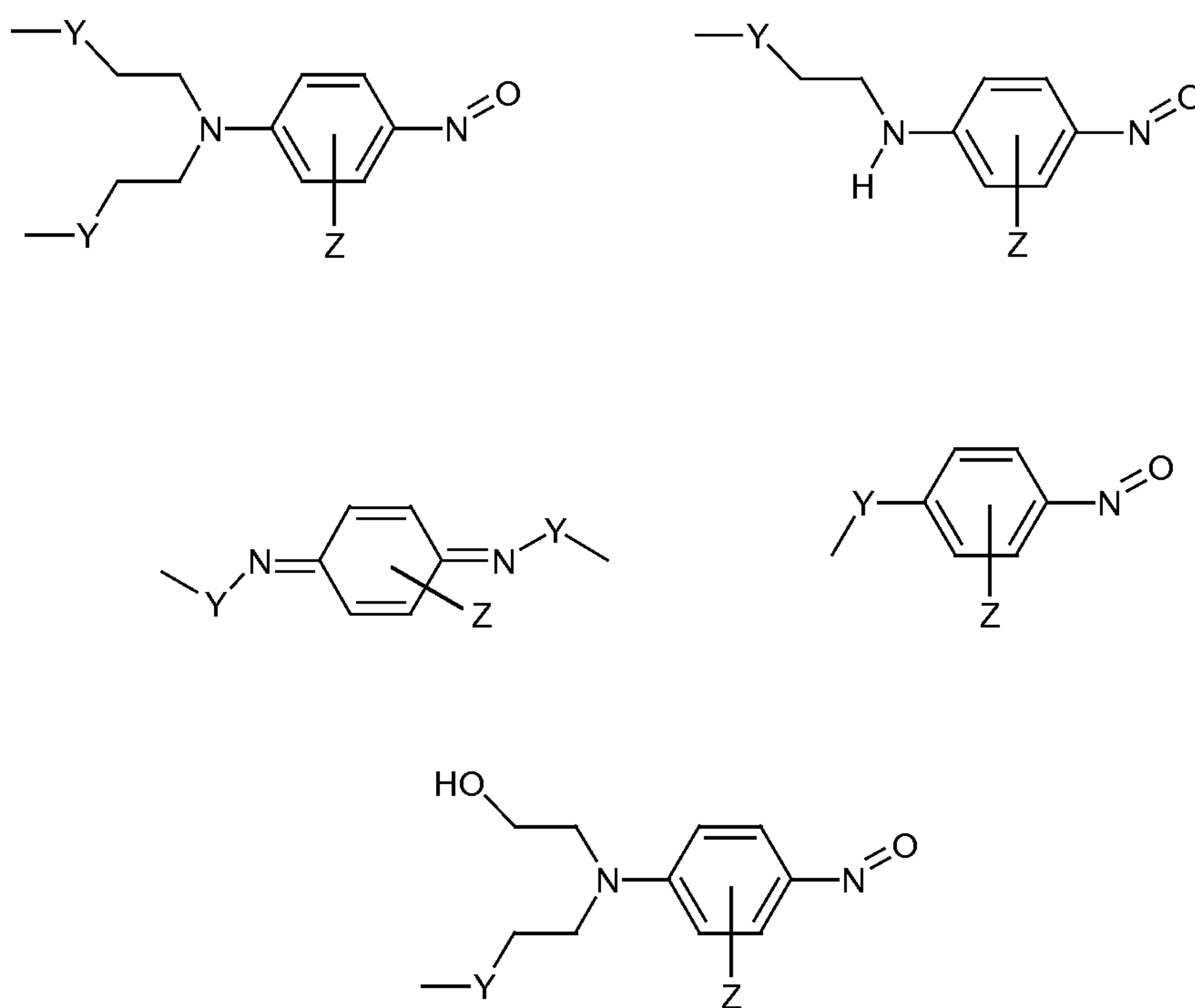
Y can be  $-O$ ,  $-S$ , or  $-NH_x$  (where  $x = 1$  or  $2$ ); and

$R^3$  is a moiety comprising nitrosobenzene, quinone dioxime or quinone oxime.

[0031]  $R^3$  may be a moiety comprising nitrosoaromatic, or a nitrosoaromatic precursor as defined herein.

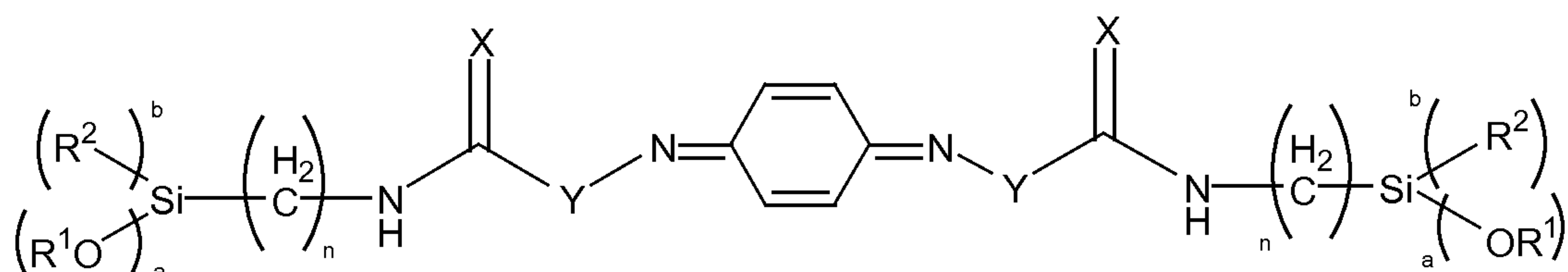
[0032]  $R^1$  may be selected from the group consisting of  $C_1$ - $C_{24}$  alkyl,  $C_3$ - $C_{24}$  acyl.  $R^1$  may be selected from the group consisting of  $C_1$ - $C_{24}$  alkyl,  $C_3$ - $C_{24}$  acyl and 'a' may be 3. X may be O. Y may be O or  $-NH_x$  (where  $x = 1$ ).  $R^1$  may be selected from  $C_1$ - $C_4$  alkyl, X may be O and 'a' is 3.  $R^1$  may be selected from  $C_1$ - $C_4$  alkyl, X may be O, Y may be O and 'a' may be 3.  $R^1$  may be selected from  $C_1$ - $C_4$  alkyl, X may be O, Y may be  $-NH_x$  (where  $x = 1$ ) and 'a' may be 3.  $R^1$  may be selected from  $C_1$ - $C_4$  alkyl, X may be O, Y may be O, 'a' may be 3 and  $R^3$  may be a moiety comprising nitrosobenzene.

[0033] Structures for  $R^3$ , showing the linkage through 'Y', can include:



wherein Z indicates that the rings of the above structures can optionally be mono-, di-, tri- or tetrasubstituted with the group consisting of alkyl, cycloalkyl, alkoxy, aralkyl, alkaryl, arylamine, arylnitroso, amino, hydroxy, halogen and combinations thereof, and further wherein the substituents can either be the same or different on each carbon atom of the ring. Such substitutions may be possible provided there is no interference with effective bonding or curing of the compositions. For example, provided there is no interference with the generation of a nitrosobenzene compound *in-situ*.

[0034] A compound according to the present invention may have the general structure:



where n can be 1-5;

'a' can be 1-3 and 'b' can be 0-2; 'a' can be 1-3 and 'b' can be 0-2; but if a = 3, b = 0; or if a = 2, b = 1; so that at least one alkoxy group is present;

R<sup>1</sup> can be selected from the group consisting of H, C<sub>1</sub>-C<sub>24</sub> alkyl, C<sub>3</sub>-C<sub>24</sub> acyl, preferably from C<sub>1</sub>-C<sub>4</sub> alkyl and wherein when a ≥ 1 at least one R<sup>1</sup> is not hydrogen; and

R<sup>2</sup> can be selected from C<sub>1</sub>-C<sub>24</sub> alkyl and C<sub>3</sub>-C<sub>24</sub> acyl, preferably from C<sub>1</sub>-C<sub>4</sub> alkyl.

X can be O or S;

Y can be -O, -S, or -NH<sub>x</sub> (where x = 1 or 2).

[0035] R<sup>1</sup> may be selected from the group consisting of C<sub>1</sub>-C<sub>24</sub> alkyl, C<sub>3</sub>-C<sub>24</sub> acyl. R<sup>1</sup> may be selected from the group consisting of C<sub>1</sub>-C<sub>24</sub> alkyl, C<sub>3</sub>-C<sub>24</sub> acyl and 'a' may be 3. X may be O. Y may be O or -NH<sub>x</sub> (where x = 1). R<sup>1</sup> may be selected from C<sub>1</sub>-C<sub>4</sub> alkyl, X may be O and 'a' is 3. R<sup>1</sup> may be selected from C<sub>1</sub>-C<sub>4</sub> alkyl, X may be O, Y may be O and 'a' may be 3. R<sup>1</sup> may be selected from C<sub>1</sub>-C<sub>4</sub> alkyl, X may be O, Y may be -NH<sub>x</sub> (where x = 1) and 'a' may be 3. R<sup>1</sup> may be selected from C<sub>1</sub>-C<sub>4</sub> alkyl, X may be O, Y may be O, n may be 3 and 'a' may be 3.

[0036] In a further aspect the invention provides for oligomeric and co-oligomeric compounds composed of monomers comprising:

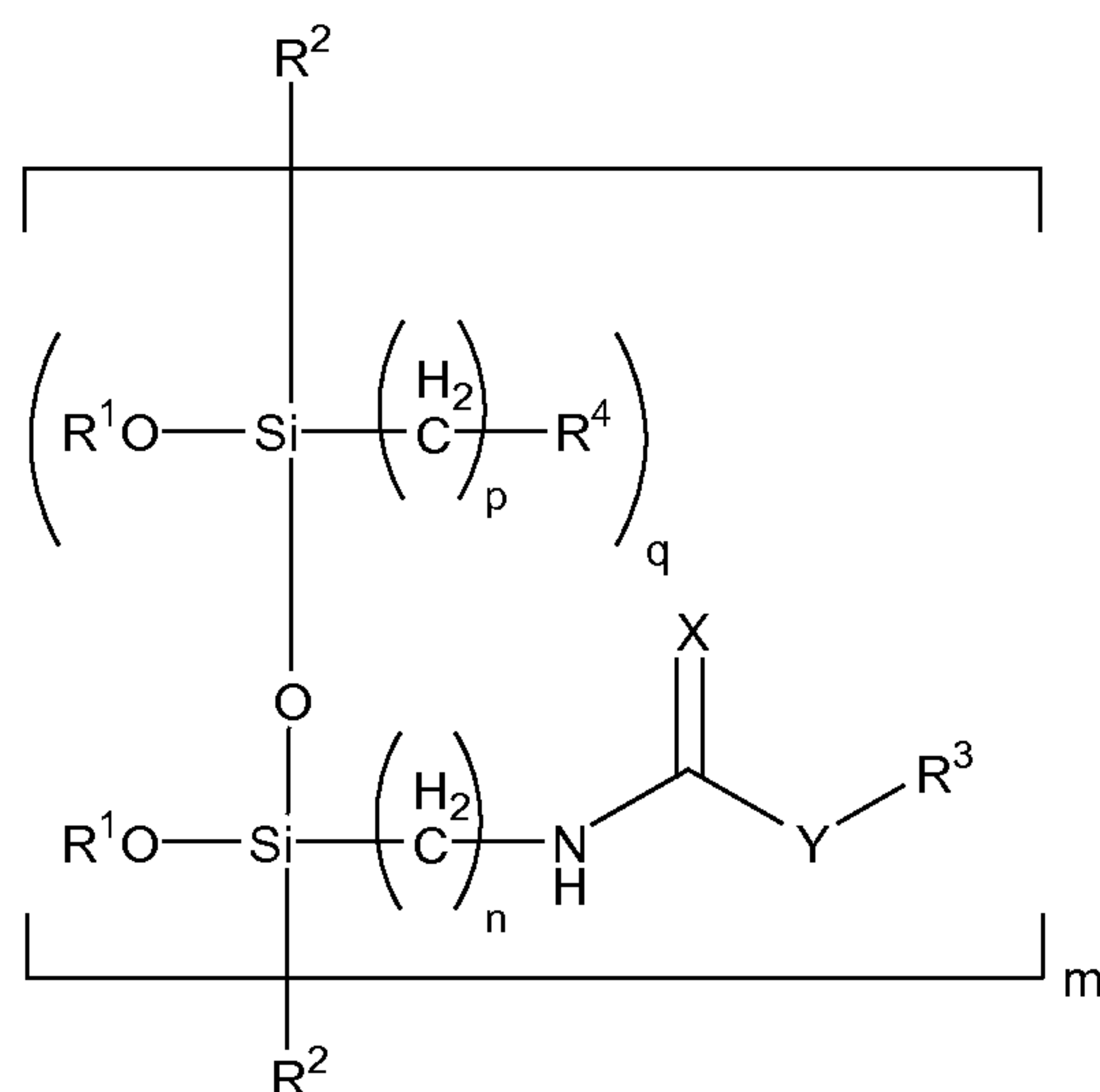
- a) at least one alkoxy silane moiety; and
- b) at least one moiety selected from an aromatic nitroso or an aromatic nitroso precursor and combinations thereof,

wherein a co-oligomeric compound is composed of different monomers.

[0037] The oligomeric and co-oligomeric compounds may be composed of monomers comprising:

- a) at least one alkoxy silane moiety; and
- b) at least one moiety selected from a nitrosobenzene or a nitrosobenzene precursor and combinations thereof.

[0038] Such oligomeric and co-oligomeric compounds may be of the general formula:



wherein m can be 1-100; n can be 1-5; p can be 1-5; q can be 0-50; and if q = 0, m ≥ 2; R<sup>1</sup> can be selected from the group consisting of H, C<sub>1</sub>-C<sub>24</sub> alkyl, C<sub>3</sub>-C<sub>24</sub> acyl, and preferably from C<sub>1</sub>-C<sub>4</sub> alkyl;

R<sup>2</sup> can be selected from the group consisting of OR<sup>1</sup>, C<sub>1</sub>-C<sub>24</sub> alkyl and C<sub>3</sub>-C<sub>24</sub> acyl, and wherein when R<sup>2</sup> = OR<sup>1</sup> at least one R<sup>1</sup> is not hydrogen;

R<sup>4</sup> can be selected from the group consisting of acrylate, aldehyde, amino, anhydride, azide, maleimide, carboxylate, sulphonate, epoxide, ester functional, halogens, hydroxyl, isocyanate or blocked isocyanate, sulfur functional, vinyl and olefin functional, or polymeric structures;

X can be O or S;

Y can be -O, -S, or -NH<sub>x</sub> (where x = 1 or 2); and

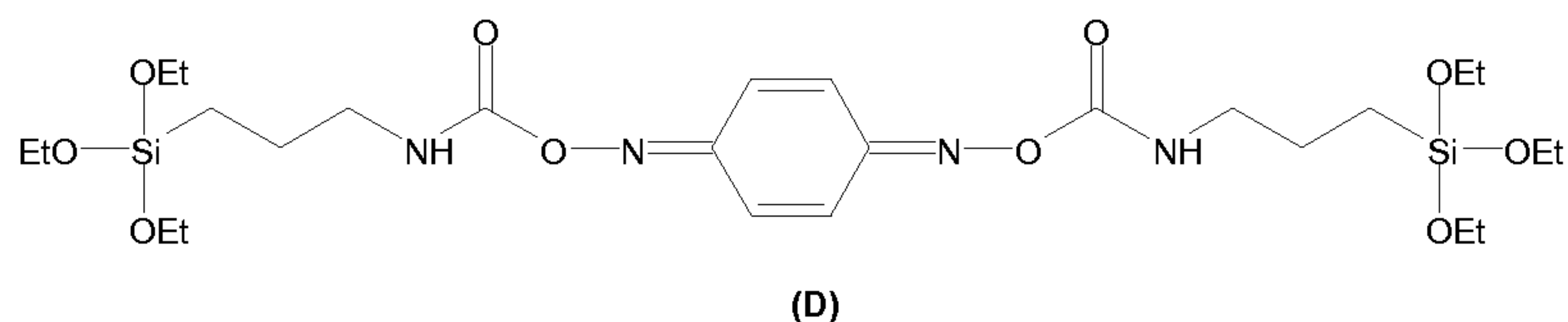
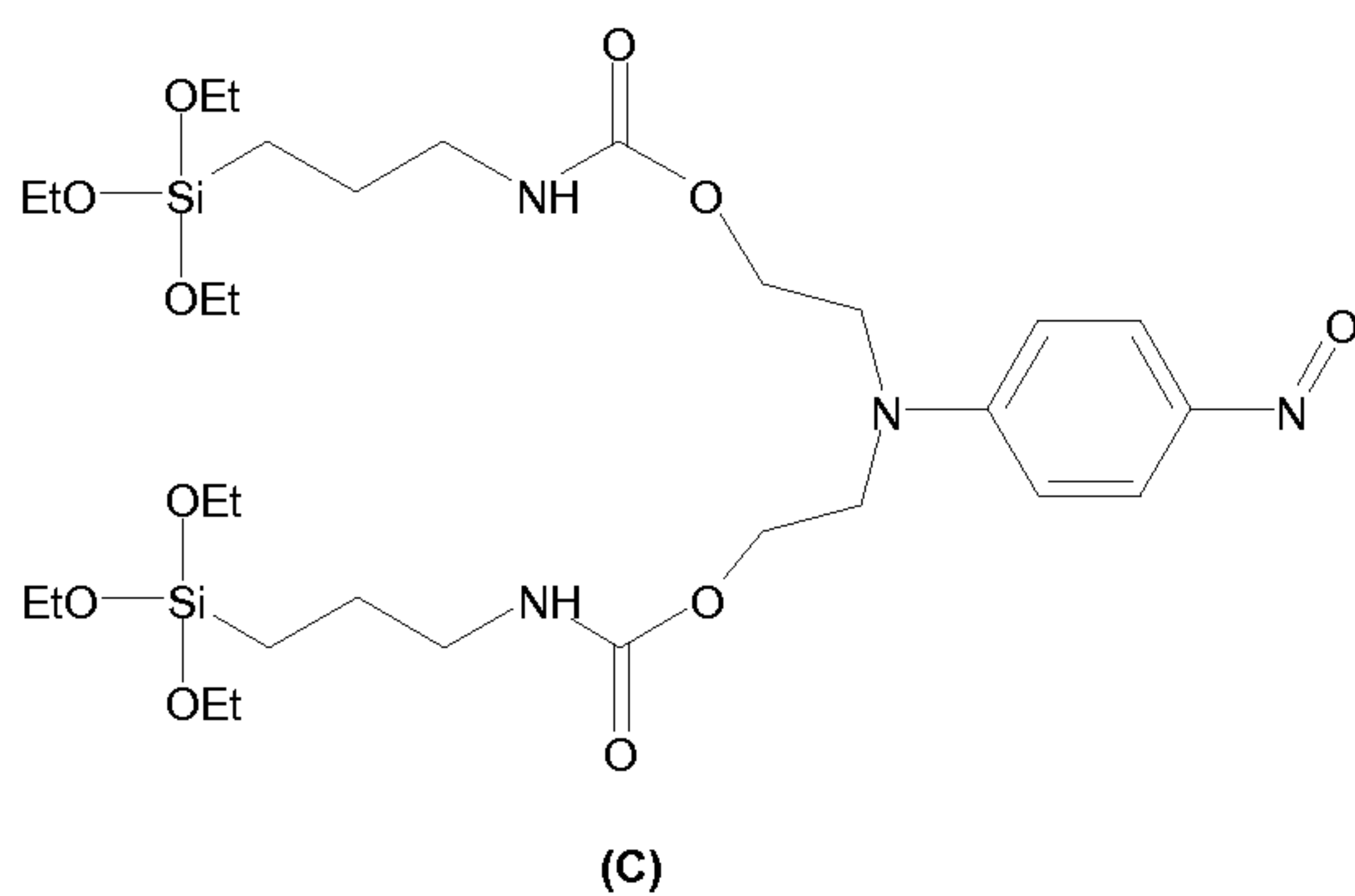
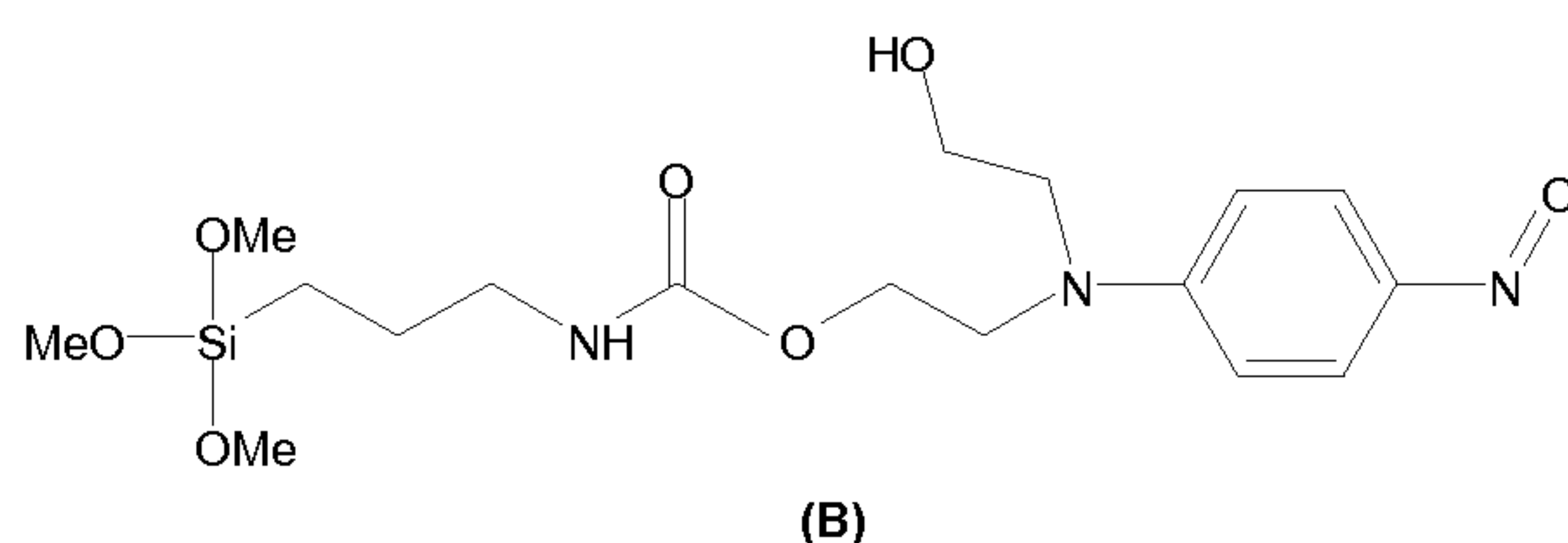
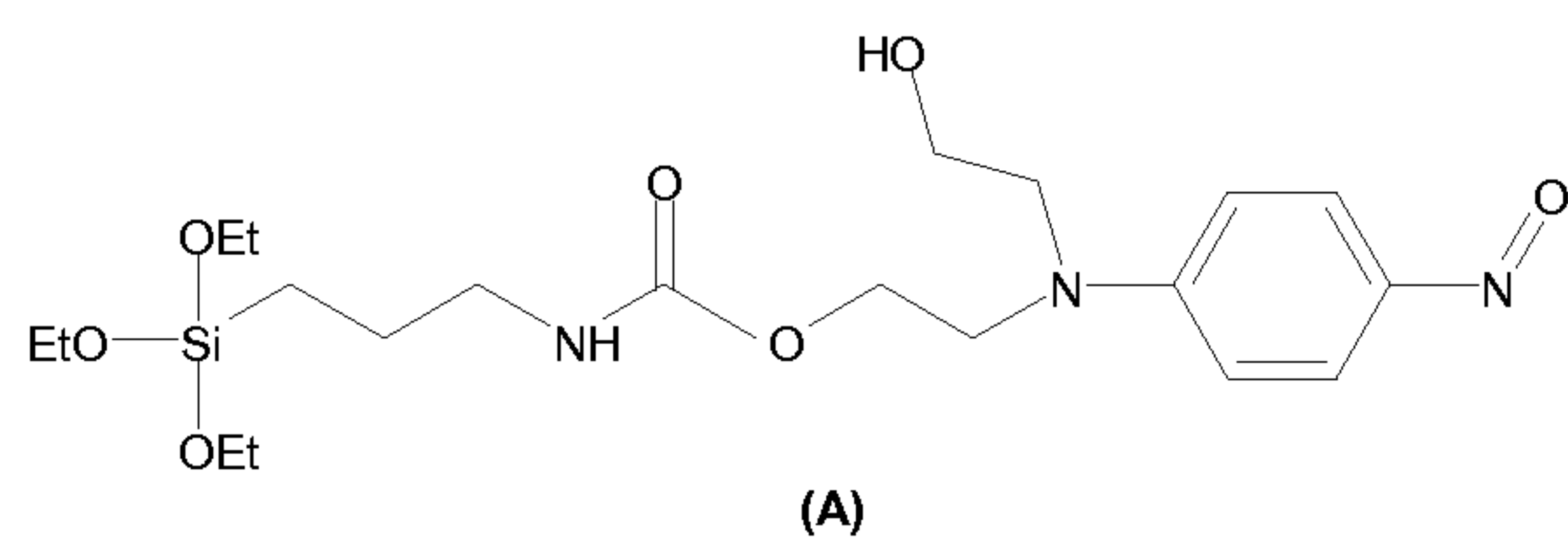
R<sup>3</sup> is a moiety comprising nitrosobenzene, quinone dioxime or quinone oxime.

[0039] R<sup>3</sup> may be a moiety comprising nitrosoaromatic, or a nitrosoaromatic precursor as defined herein.

[0040] R<sup>1</sup> may be selected from the group consisting of C<sub>1</sub>-C<sub>24</sub> alkyl, C<sub>3</sub>-C<sub>24</sub> acyl. R<sup>1</sup> may be selected from the group consisting of C<sub>1</sub>-C<sub>24</sub> alkyl, C<sub>3</sub>-C<sub>24</sub> acyl and R<sup>2</sup> may be OR<sup>1</sup>. X may be O. Y may be O or -NH<sub>x</sub> (where x = 1). R<sup>1</sup> may be selected from C<sub>1</sub>-C<sub>4</sub> alkyl, X may be O and R<sup>2</sup> may be OR<sup>1</sup>. R<sup>1</sup> may be selected from C<sub>1</sub>-C<sub>4</sub> alkyl, X may be O, Y may be O and R<sup>2</sup> may be OR<sup>1</sup>. R<sup>1</sup> may be selected from C<sub>1</sub>-C<sub>4</sub> alkyl, X may be O, Y may be -NH<sub>x</sub> (where x = 1) and R<sup>2</sup> may be OR<sup>1</sup>. R<sup>1</sup> may be selected from C<sub>1</sub>-C<sub>4</sub>

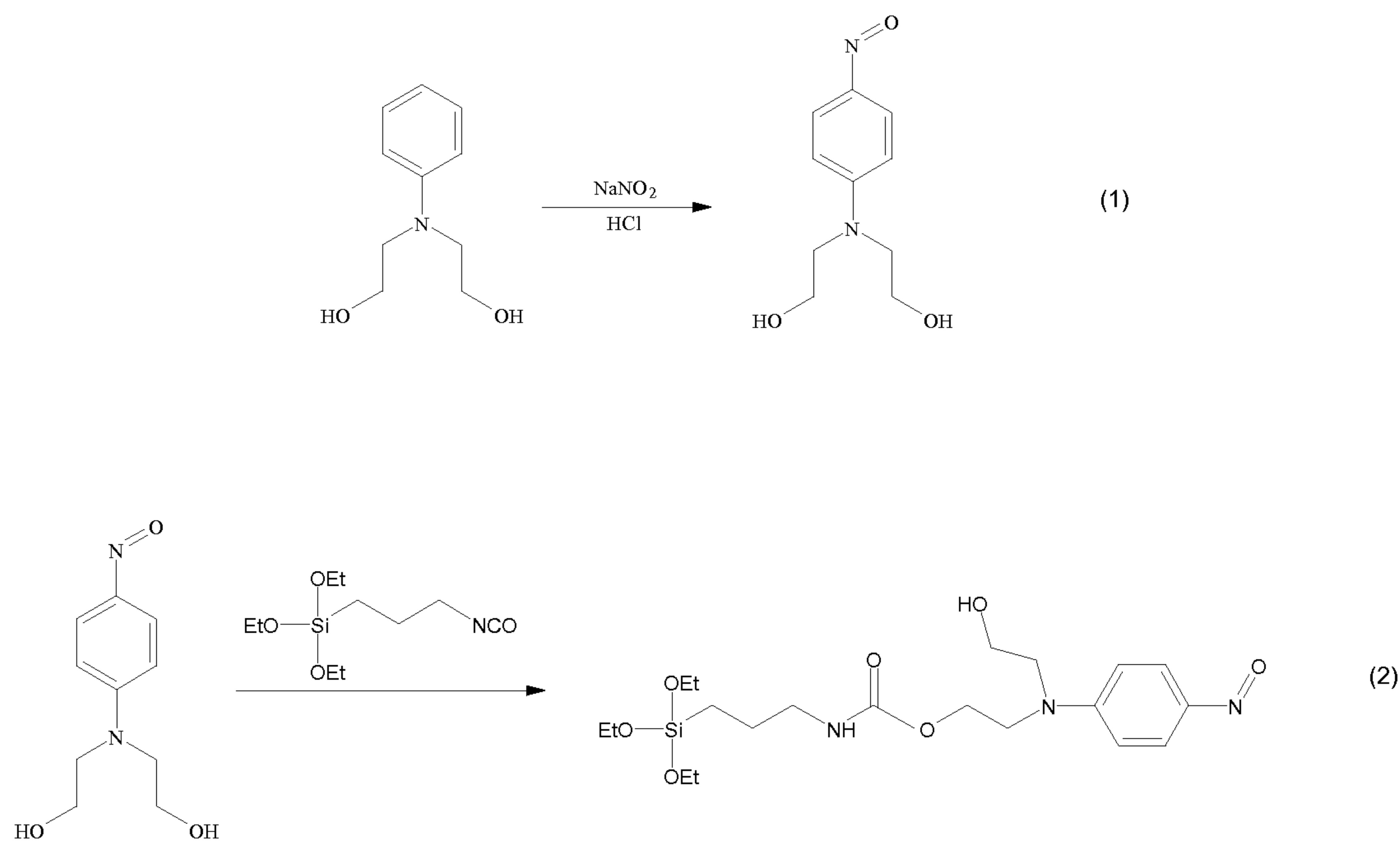
alkyl, X may be O, Y may be O, n may be 3, R<sup>2</sup> may be OR<sup>1</sup> and R<sup>3</sup> may be a moiety comprising nitrosobenzene. R<sup>1</sup> may be selected from C<sub>1</sub>-C<sub>4</sub> alkyl, X may be O, Y may be O, n may be 3, R<sup>2</sup> may be OR<sup>1</sup>, R<sup>3</sup> may be a moiety comprising nitrosobenzene, q may be 0, and m may be  $\geq 2$ . R<sup>1</sup> may be selected from C<sub>1</sub>-C<sub>4</sub> alkyl, X may be O, Y may be O, n may be 3, R<sup>2</sup> may be OR<sup>1</sup>, R<sup>3</sup> may be a moiety comprising nitrosobenzene, q may be 0, m may be  $\geq 2$ , and R<sup>4</sup> may be vinyl or ester.

[0041] Specific examples of compounds of the present invention include the following:



[0042] The reaction scheme for the synthesis of (A) is below (all compounds are made in an analogous method).

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**[0043]** It will be appreciated that compositions suitable for bonding metal to rubber may be formulated utilising appropriate amounts of one or more of the so-described compounds.

**[0044]** Accordingly, a composition for bonding substrates together is also provided where the composition comprises:

- (i) at least one compound comprising;
  - a) at least one alkoxy silane moiety; and
  - b) at least one moiety selected from an aromatic nitroso or an aromatic nitroso precursor and combinations thereof; and

(ii) a suitable carrier vehicle for the compound. It will be appreciated that any suitable carrier vehicle may be utilised. It is desirable that the carrier vehicle should be environmentally friendly. Such compositions are suitable for use in bonding a substrate such as a metal substrate to a natural or synthetic rubber.

**[0045]** The composition for bonding substrates together may comprise

- (i) at least one compound comprising;
  - a) at least one alkoxy silane moiety; and
  - b) at least one moiety selected from a nitrosobenzene or a nitrosobenzene precursor and combinations thereof; and
- (ii) a suitable carrier vehicle for the compound.

[0046] The compound comprising the at least one alkoxy silane moiety and the at least one moiety selected from an aromatic nitroso or an aromatic nitroso precursor may be present in an amount of 1 to 20% w/w of the total composition. Suitably, the at least one aromatic nitroso compound precursor may be present in an amount of 1 to 15% w/w, for example 4 to 12% w/w. The at least one aromatic nitroso compound precursor may be present in 6% w/w of the total composition.

[0047] Compositions of the present invention may find utility in any application where it is desirable to form an aromatic nitroso moiety *in-situ*. Similarly, compositions of the present invention may find utility in any application where it is desirable to form an aromatic dinitroso moiety *in-situ*. It will be appreciated that within these compositions the compound can react *in-situ* to form a nitrosobenzene moiety. It is also contemplated that the compound can react *in-situ* to form a dinitrosobenzene moiety. For example, for particularly good bonding it may be desirable for the compound to react *in-situ* to form a *para*-nitrosophenol moiety.

[0048] Compositions of the present invention may be one-part compositions. Compositions of the present invention may be two-part compositions.

[0049] Also provided is a process for bonding two substrates together comprising applying the so-described composition to a bonding surface of at least one of the substrates and bringing the bonding surfaces of the substrates together. For example a first substrate may be constructed from a natural or synthetic rubber to be bonded to another substrate. The other or second substrate may be a metallic substrate. Generally, the alkoxy silane moiety of the compound will anchor to a metal surface. The moiety selected from an aromatic nitroso or an aromatic nitroso precursor will generally become anchored to the rubber. Similarly, the moiety selected from a nitrosobenzene or a nitrosobenzene precursor will generally become anchored to the rubber. Accordingly, each end of the molecule is functionalised and assists in bonding the materials together with a strong and durable bond.

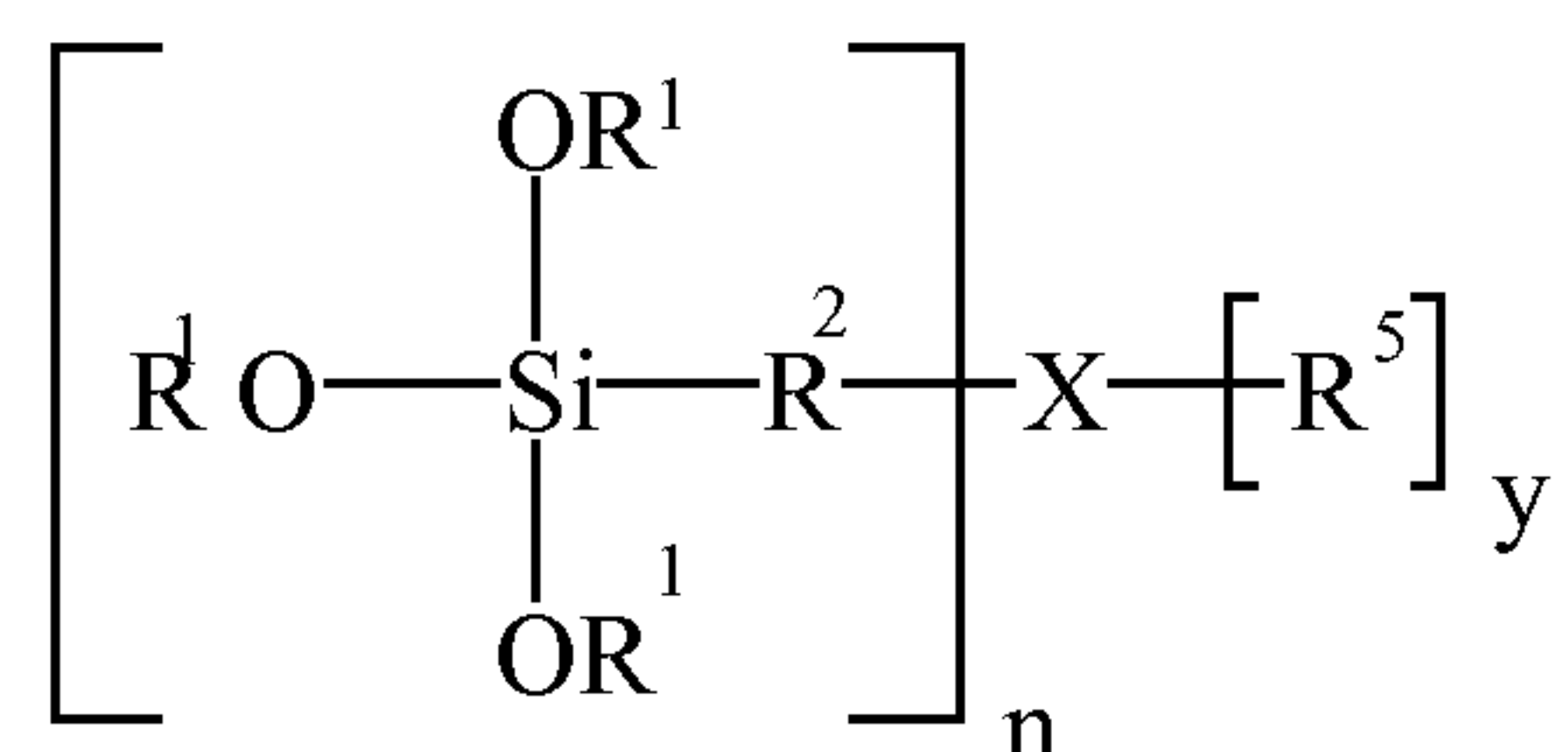
[0050] Thus, a metal coated with an adhesive composition as so described may be adhered to a polymeric material, for example a rubber composition, by applying the polymeric material in an uncured state onto the metal coated with the adhesive composition and curing the polymeric material thereon to bond it to the metal. In the case of a rubber polymeric material the uncured rubber may be vulcanized *via* heat and

pressure over a period of time to cure the rubber, resulting in bonding of the rubber to the metal.

**[0051]** Such bonding to metals is achieved through the nitroso groups which are capable of reacting with polymers, in particular a polymer with alkene/allylic functionality within the polymer chain. For example, diene or allylic functionality within the polymer chain. Such a reaction produces a variety of cross-links for example between the nitroso group and a rubber material. The materials of the invention are thought to reduce free nitroso groups as the nitroso group is within a molecular structure. In the reaction of the nitroso and the silane, the nitroso reacts with alkene functionality within the natural rubber while the silane forms the bond with the metal.

**[0052]** Dinitrosobenzene is known to be a very effective cross-linker in adhesive formulations, and often results in bonds that are characterised by high permanent strength and by high resistance to aggressive media. However, unreacted free nitroso materials such as dinitrosobenzene can give rise to continuing vulcanization in the event of composition subsequent heat treatment, resulting in unwanted embrittlement of the bond. For embodiments of the present invention that do not provide for the release of dinitrosobenzene, the latter problem may be alleviated due to the fact that the reaction product of the nitroso and the silane would contain no free nitroso materials such as dinitrosobenzene and thus would not be free to undergo further vulcanization. Reducing the hazards associated with conventional systems is also important.

**[0053]** Combinations of silanes may be employed in the present invention. For example one or more additional silanes may be included within compositions of the present invention. These silanes are generally of the formula:



where:

n is either 1 or 2;

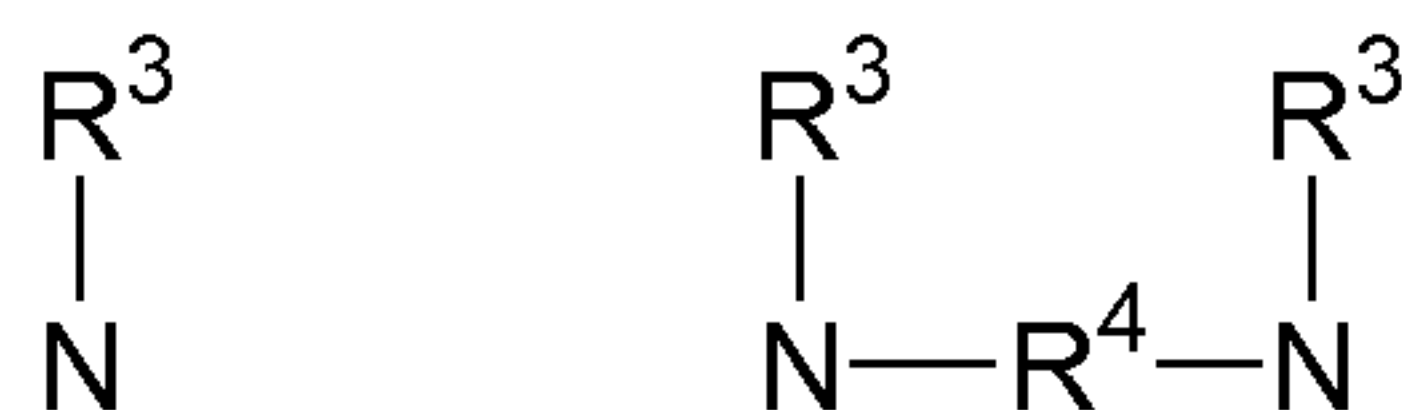
y = (2-n)

each R<sup>1</sup> can be selected from C<sub>1</sub>-C<sub>24</sub> alkyl or C<sub>2</sub>-C<sub>24</sub> acyl;

each R<sup>2</sup> can be selected from C<sub>1</sub>-C<sub>30</sub> aliphatic groups, substituted C<sub>3</sub>-C<sub>30</sub> aromatic groups, or unsubstituted C<sub>3</sub>-C<sub>30</sub> aromatic groups;

$R^5$  can be selected from hydrogen,  $C_1$ - $C_{10}$  alkylene,  
 $C_1$ - $C_{10}$  alkylene substituted with one or more amino groups,  $C_2$ - $C_{10}$  alkenylene  
substituted with one or more amino groups,  $C_6$ - $C_{10}$  arylene, or  $C_7$ - $C_{20}$   
alkylarylene;

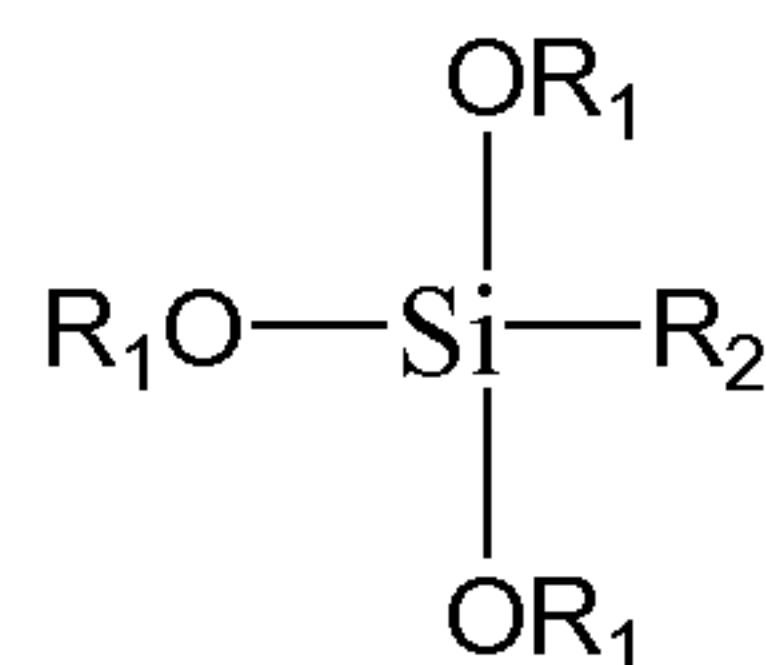
X is optional and is either:



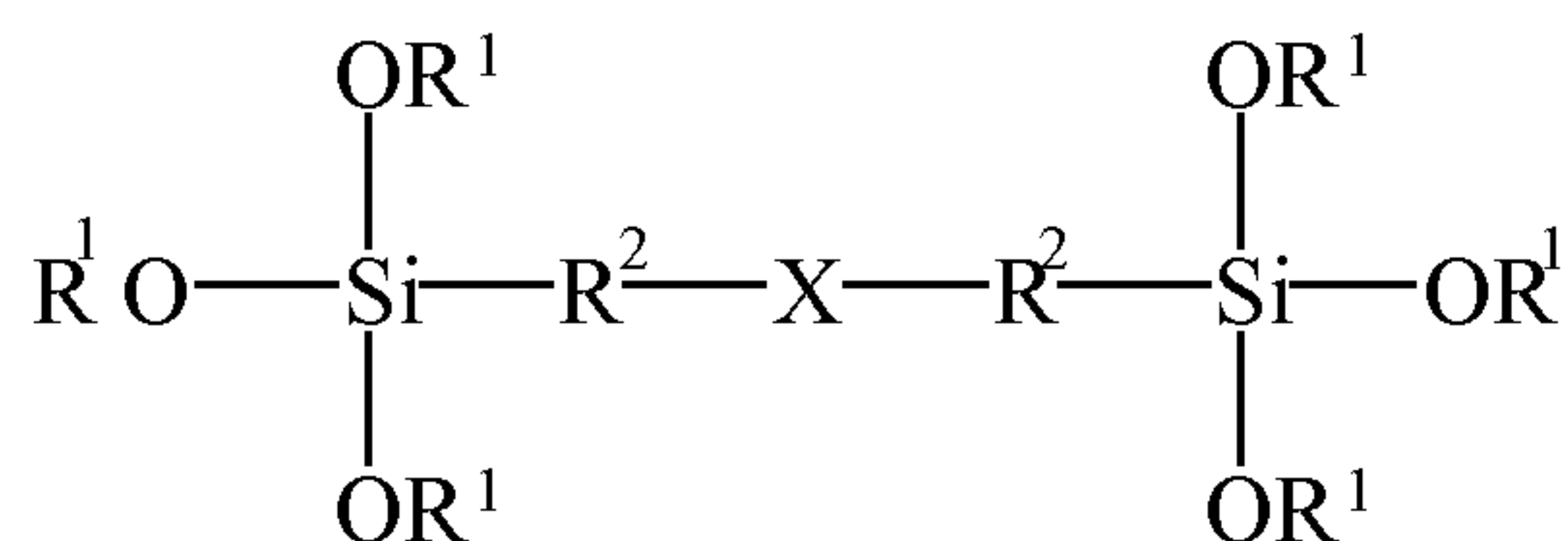
where each  $R^3$  can be selected from hydrogen,  $C_1$ - $C_{30}$  aliphatic groups, or  $C_6$ - $C_{30}$   
aromatic groups; and

$R^4$  can be selected from  $C_1$ - $C_{30}$  aliphatic groups, or  $C_6$ - $C_{30}$  aromatic groups; and  
wherein when  $n = 1$ , at least one of the  $R^3$  and the  $R^5$  is not hydrogen.

[0054] In one embodiment, X is present. As will be appreciated, when X is absent  
the silane may be of the general formula:



[0055] Preferred silanes include bis-silyl silanes such as those having two  
trisubstituted silyl groups. The substituents may be individually chosen from  $C_1$ - $C_{20}$   
alkoxy,  $C_6$ - $C_{30}$  aryloxy and  $C_2$ - $C_{30}$  acyloxy. Suitable bis-silyl silanes for use within the  
present invention include:



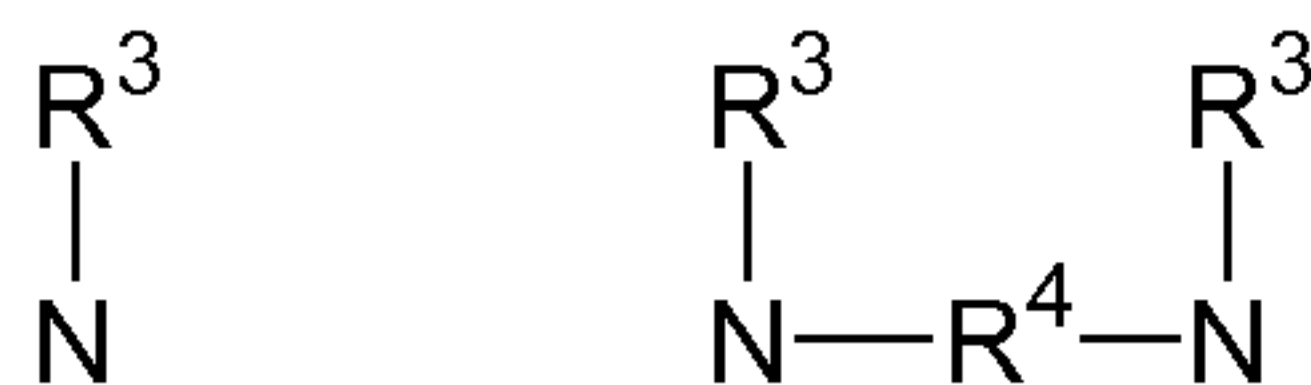
where:

each  $R^1$  can be selected from  $C_1$ - $C_{24}$  alkyl or  $C_2$ - $C_{24}$  acyl;

each  $R^2$  can be selected from the group consisting  $C_1$ - $C_{20}$  aliphatic groups, or  $C_6$ - $C_{30}$   
aromatic groups;

X is optional and is either:

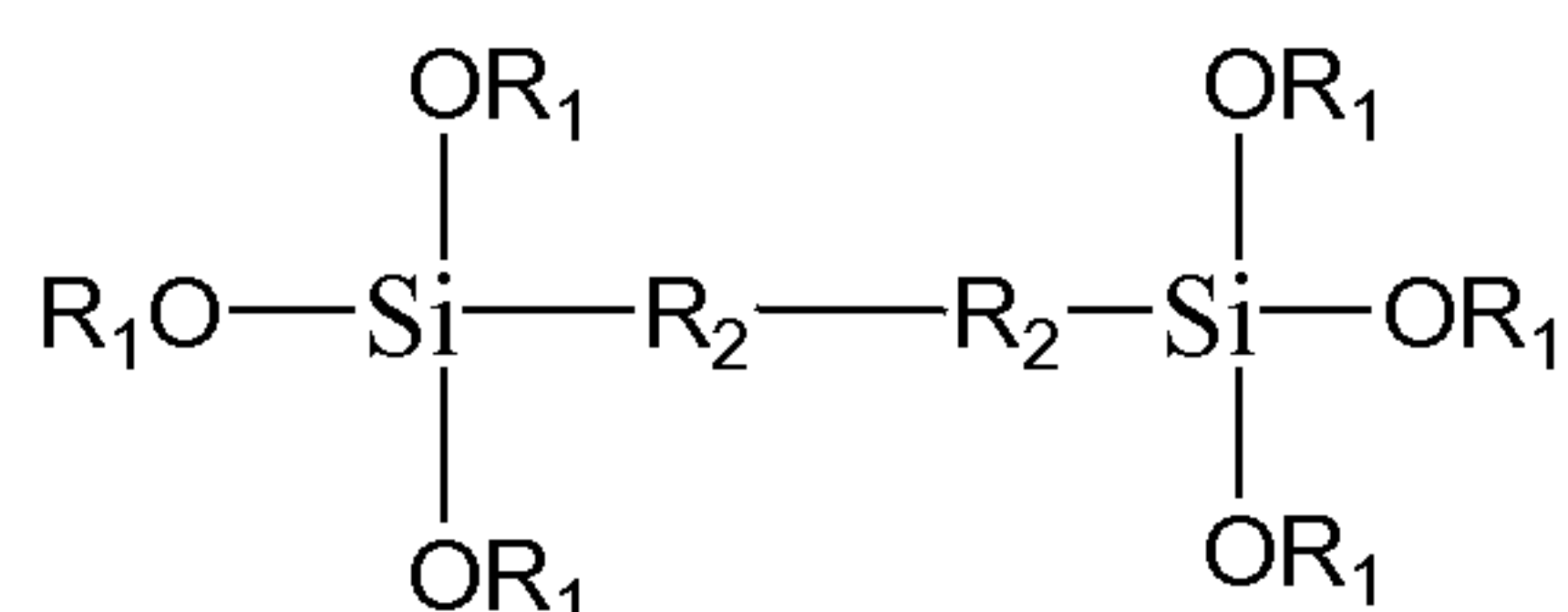
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where each  $\text{R}^3$  can be selected from hydrogen,  $\text{C}_1$ - $\text{C}_{20}$  aliphatic groups, or  $\text{C}_6$ - $\text{C}_{30}$  aromatic groups; and

$\text{R}^4$  can be selected from  $\text{C}_1$ - $\text{C}_{20}$  aliphatic groups or  $\text{C}_6$ - $\text{C}_{30}$  aromatic groups.

[0056] In one embodiment, X is present. As will be appreciated, when X is absent the *bis*-silane may be of the general formula:



[0057] Examples of some bis-silyl aminosilanes embraced by the present invention include: bis-(trimethoxysilylpropyl)amine, bis-(triethoxysilylpropyl)amine, bis-(triethoxysilylpropyl) ethylene diamine, *N*-[2-(vinylbenzylamino)ethyl]-3-aminopropyltrimethoxy silane, and aminoethyl-aminopropyltrimethoxy silane.

Such additional silanes may be included in the range from 1:3 to 3:1 relative to the compounds of the present invention. Such mixing can result in excellent rubber-to-metal bonding.

[0058] In particular, the inclusion of the amino bis(propyltrimethoxysilane) in addition to the nitroso silane enhances the rubber to metal bond strength significantly. It is thought that the amino bis(propyltrimethoxysilane) has multiple functions within the formulation. This includes aiding the film forming and “wetting” of the metal surface.

[0059] The silane may be present in an amount of 1 to 10% w/w of the total composition. Suitably, the silane may be present in an amount of 1 to 5% w/w, for example 1 to 3% w/w. The silane may be present in 3% w/w of the total composition.

[0060] A significant difference between the present invention and the prior art is that in the present invention the silanes can be “significantly unhydrolysed”, meaning that they are utilised in an unhydrolysed state. This arises as the materials can be applied neat and/or without any water being present.

[0061] The amino silane(s) and nitroso silane(s) may be independently hydrolysed and/or mixed and hydrolysed to form the final silane solution. 5% water solutions are generally sufficient to effectively hydrolyse the silanes. Alternatively the silanes can be

added to a neat solvent, used as received, without the addition of water for intentional promotion of hydrolysis.

[0062] Generally, the final silane solution applied to the metal substrate may vary in the silane concentration and ratio (amino silane to nitroso silane) over a wide range and still provide beneficial results. The final solution should contain a total silane concentration of at least approximately 0.1% by volume, *i.e.* the concentration of the combination of amino silanes and nitroso silanes in the final solution. Solutions having a silane concentration of between about 0.1% and about 10% by volume generally provide strong bonding without waste of valuable silanes.

[0063] Excellent adhesion between polymeric materials, such as rubber compositions, and metals, with minimal waste of silane solution may be realized through the use of the compounds and compositions as so described. With reference to their use in adhesive applications, the compositions of the present invention are generally thinner than the compositions present in the traditional adhesive systems for rubber to metal bonding, without any loss in performance characteristics. Composition thickness may be determined by the concentration of the reaction product of the nitroso and the silane, and are in the range of 0.1 to 12  $\mu\text{m}$ , and more preferably in the range of 0.5 to 10  $\mu\text{m}$ .

[0064] Many different metals may be treated with the composition described in this invention, and may be bonded to polymeric materials. These metals include, but are not limited to, zinc and zinc alloys such as zinc-nickel and zinc-cobalt alloys, metal substrates having zinc-containing coatings, steel and in particular cold rolled and carbon steel, aluminium and aluminium alloys, copper and copper alloys such as brass, and tin and tin alloys including metal substrates having tin-containing coatings.

### **Detailed Description**

[0065] The rubber composition involved in rubber to metal bonding using the described methods in the current invention may further include known additives common to rubber compositions. These include reinforcing carbon blacks; inactive fillers such as calcium carbonates, chalks, talcs, or metal oxides; accelerator systems; vulcanization retarders; promoters such as zinc oxide or stearic acid; plasticizers such as aromatic, paraffinic, naphthenic and synthetic mineral oils; ageing, light-protecting ozone-protecting, fatigue, coloration, and processing auxiliaries; and sulfur. Commonly

these additives may be present at a quantity of about 0.1 parts to about 80 parts per 100 parts by weight of the rubber composition.

[0066] Hydrolysis, formation of silanol groups, *i.e.* SiOH, will generally occur efficiently within the pH range of 3 – 7. At a pH above or below this range, silane condensation may occur by a process where the silanol self-condenses to form a siloxane. During this process the hydroxyl molecules of the adjacent molecules react with one another to eliminate molecules of water and form a cross-linked siloxane structure containing -Si-O-Si-O-Si- functionality.

[0067] To accelerate silane hydrolysis and inhibit silane condensation during the hydrolysis step, the pH of the silane solution may be maintained below about 7 and preferably in the mildly acidic range from about 4 to 6.5 (particularly for hydrolysis of the bis-silyl aminosilanes). This can be achieved by addition of one or more compatible acids. For example, organic acids such as acetic acid, oxalic acid, formic acid, propionic acid, may be added to the hydrolysing solution to adjust the pH. Sodium hydroxide, or other compatible bases, may also be used, when needed, to raise the pH of the silane solution. Some silanes provide a mildly acidic pH solution when mixed with water and may not need a pH adjustment to accelerate hydrolysis. The pH ranges discussed with respect to preparing the silane-hydrolyzing solutions should not be confused with the pH of the final silane solution applies to the metal substrate.

[0068] The hydrolysing silane solutions may further include one or more of compatible solvents. Alcohols are generally used for solubilising and hydrolysing silanes. Suitable alcohols include, without limitation, methanol, ethanol, n-propanol, isopropanol, n-butanol, sec-butanol, tert-butanol, and longer aliphatic alcohols. The ratio of water to solvent in the hydrolysed silane solution (as applied to the metal substrate, by volume) may be between about 1:99 and about 99:1, and preferably between 1:1 and 1:20.

[0069] Prior to application of the silane solution, the metal surface to be coated may be cleaned to allow better adhesion. For example, cleaning with solvent or alkaline material. Application can then be conducted by a variety of methods, including dipping, spraying, brushing or wiping the solution onto the metal. It has been suggested that for improving rubber adhesion the coating remain partially cross-linked prior to vulcanisation. For this reason, the coating is usually air dried at room temperature as

heat drying can cause a higher degree of cross-linking that will result in poorer adhesion between the rubber and the metal surface.

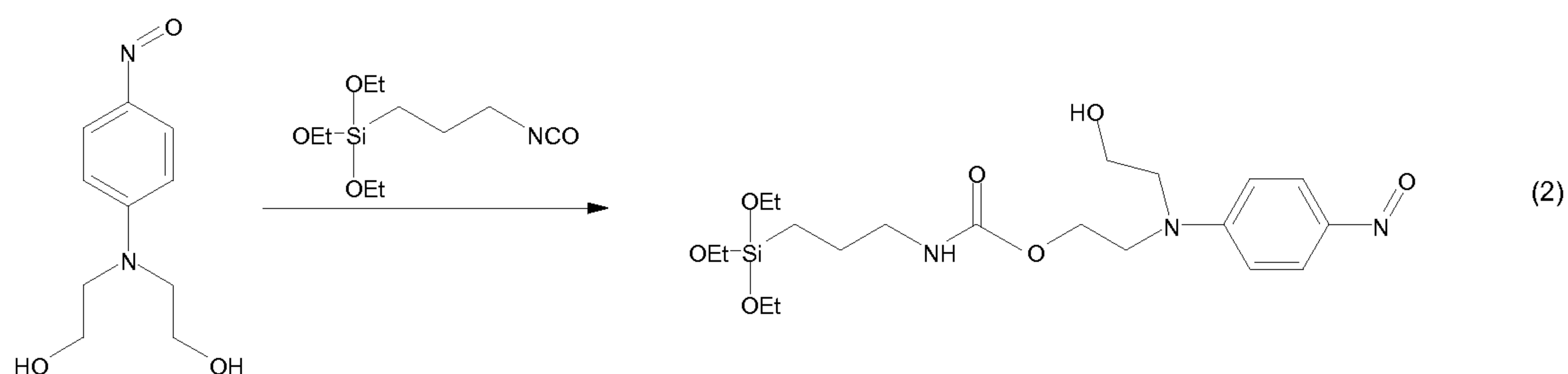
[0070] Compounds of the invention were made as set out below:

### Examples

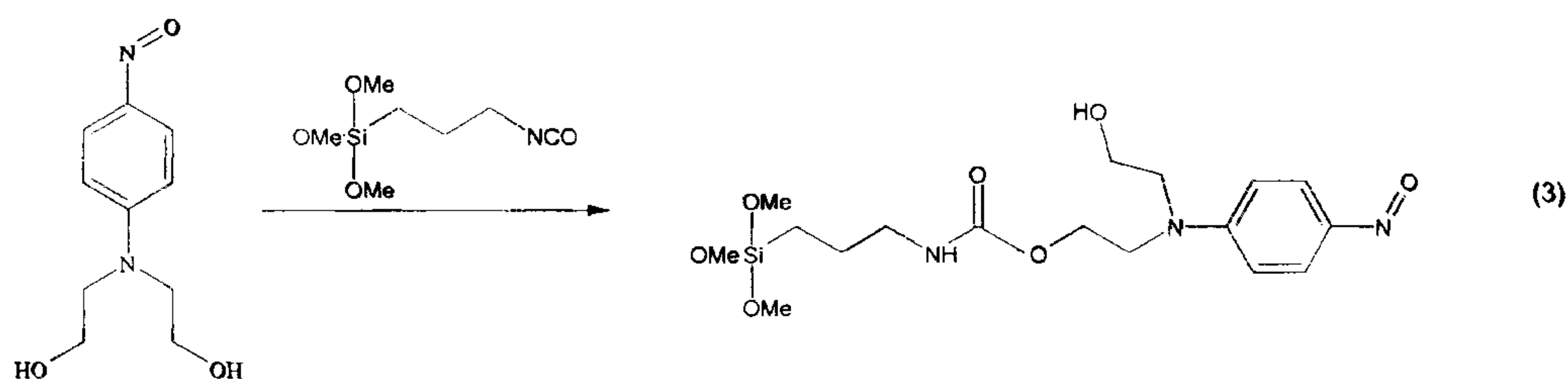
[0071] Compounds A, B, C and D (above) were synthesised according to the following experimental procedure and as illustrated in the reaction scheme above.

[0072] **Reaction (1)** (*vide supra*) was carried out as outlined in J.J D'Amico, C.C. Tung and L.A. Walker, *J. Am. Chem. Soc.*, 5957 (1959).

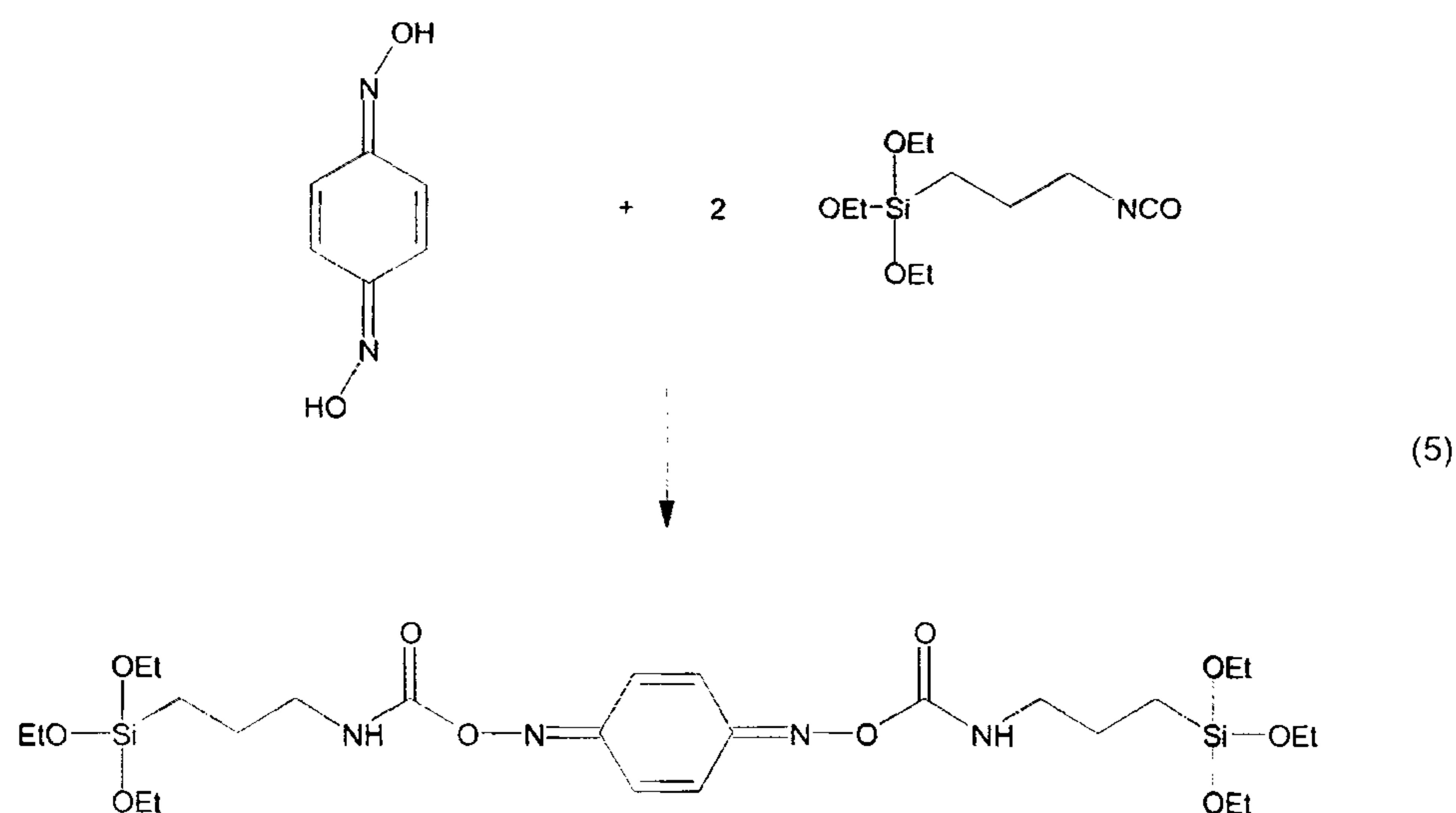
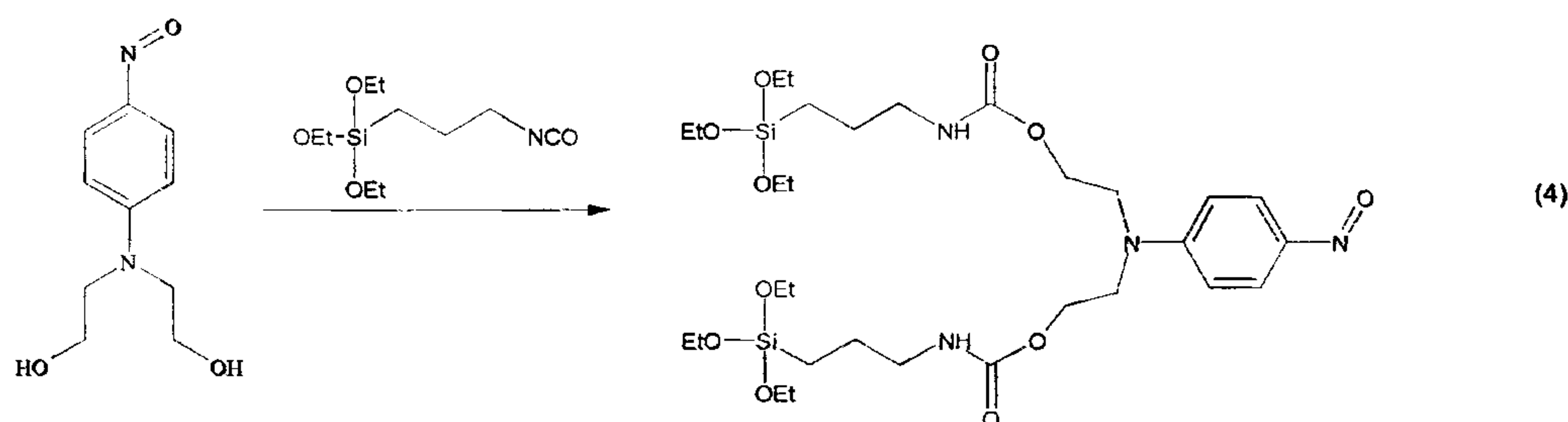
[0073] **Reaction (2):**  $\gamma$ -Isocyanatopropyltriethoxysilane (GE Bayer Silicones A-1310) (2.35 g, 9.5 mmol) was solvated in 10 mL of anhydrous THF in a 50 mL round bottom flask. The reaction flask was flushed with nitrogen and charged with *N,N*-bis-(2-hydroxyethyl)-4-nitroso-aniline (2 g, 9.5 mmol), followed by a catalytic quantity of dibutyltin dilaurate (1.5  $\mu$ mol). The reaction was refluxed for an additional 2 hours under nitrogen. Consumption of the isocyanate (2275  $\text{cm}^{-1}$ ) was monitored using infrared spectroscopy. The solvents were removed under reduced pressure to give the product in a quantitative yield.



[0074] **Reaction 3:**  $\gamma$ -Isocyanatopropyltrimethoxysilane (ABCR GmbH) (1.5g, 7.3 mmol) was solvated in 8 mL of anhydrous THF in a 50 mL round bottom flask. The reaction flask was flushed with nitrogen and charged with *N,N*-bis-(2-hydroxyethyl)-4-nitroso-aniline (1.53 g, 7.3 mmol), followed by a catalytic quantity of dibutyltin dilaurate (1  $\mu$ mol). The reaction was refluxed for an additional 2 hours under nitrogen. Consumption of the isocyanate (2275  $\text{cm}^{-1}$ ) was monitored using infrared spectroscopy. The solvents were removed under reduced pressure to give the product in a quantitative yield.

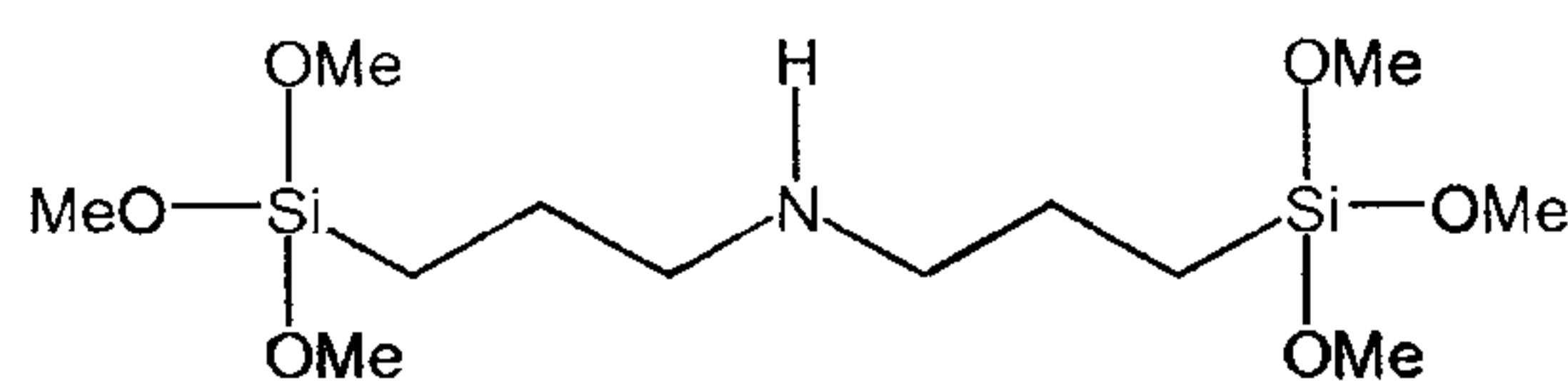


[0075] **Reaction 4:**  $\gamma$ -Isocyanatopropyltriethoxysilane (GE Bayer Silicones A-1310)<sup>TM</sup> (2.35 g, 9.5 mmol) was solvated in 10 mL of anhydrous THF in a 50 mL round bottom flask. The reaction flask was flushed with nitrogen and charged with *N,N*-bis-(2-hydroxyethyl)-4-nitroso-aniline (1 g, 4.75 mmol), followed by a catalytic quantity of dibutyltin dilaurate (1.5  $\mu$ mol). The reaction was refluxed for an additional 5 hours under nitrogen. Consumption of the isocyanate (2275  $\text{cm}^{-1}$ ) was monitored using infrared spectroscopy. The solvents were removed under reduced pressure to give the product in a quantitative yield.



[0076] **Reaction 5:**  $\gamma$ -Isocyanatopropyltriethoxysilane (GE Bayer Silicones A-1310) (10.68 g, 43.18 mmol) was solvated in 30 mL of anhydrous THF in a 100 mL round bottom flask. The reaction flask was flushed with nitrogen and charged with *p*-benzoquinone dioxime (Sigma-Aldrich) (3 g, 21.72 mmol), followed by a catalytic quantity of dibutyltin dilaurate. The reaction was refluxed for an additional 5 hours under nitrogen. Consumption of the isocyanate ( $2275\text{ cm}^{-1}$ ) was monitored using infrared spectroscopy. The solvents were removed under reduced pressure to give the product in a quantitative yield.

[0077] Formulations comprising the compounds of the invention were prepared as set out below, where compounds A to C are compounds of the invention as set out above in the Summary of the Invention. Compound E is Bis(trimethoxysilylpropyl)amine – commercially available from Sigma Aldrich. Compound E has the formula:



(E)

#### ***Natural Rubber Composition***

Tests were carried out using natural rubber of the following composition:

Ingredient	Parts by weight
Natural Rubber <sup>(a)</sup>	100
Zinc Oxide	3.5
Stearic Acid	2
Carbon Black <sup>(b)</sup>	40
Naphthenic Oil (low viscosity) <sup>(c)</sup>	5
1,2-Dihydro-2,2,4-Trimethylquinoline <sup>(d)</sup>	2
N-(1,3-dimethylbutyl)-N'-phenyl-p-phenylenediamine <sup>(e)</sup>	1
Hydrocarbon Waxes <sup>(f)</sup>	2
CBS <sup>(g)</sup>	0.7
Sulphur	2.5

<sup>(a)</sup> NR SMR CV 60; <sup>(b)</sup> SRF N762 black; <sup>(c)</sup> Oil Strukthene 410; <sup>(d)</sup> Flectol H; <sup>(e)</sup> Santoflex<sup>TM</sup> 13 (HPPD); <sup>(f)</sup> Sunproof Improved Wax; <sup>(g)</sup> Vulcanisation accelerator, N-Cyclohexyl-2-benzothiazole.

**EPDM Rubber Composition**

Tests were carried out using EPDM rubber of the following composition:

Ingredient	Parts by weight
Ethylene-Propylene-Ethylidene Norbornene (7.8% diene) <sup>(a)</sup>	25
Ethylene-Propylene-Ethylidene Norbornene (9.0% diene) <sup>(b)</sup>	72.5
Ethylene-Propylene-Dicyclopentadiene (10.5% diene) <sup>(c)</sup>	25
Carbon Black	70
Calcium Oxide	10
Stearic Acid	1
Zinc Oxide	5
Dicumyl peroxide <sup>(d)</sup>	3.75
Polyethylene Glycol <sup>(e)</sup>	4.5

<sup>(a)</sup> Buna<sup>TM</sup> EP G 3850; <sup>(b)</sup> Buna EP G 3963; <sup>(c)</sup> Trilene<sup>TM</sup> 65; <sup>(d)</sup> Dicap<sup>TM</sup> 40C; <sup>(e)</sup> Carbowax<sup>TM</sup> 400

**Compositions Used in Natural Rubber to Metal Bonding**

Formulation parts % by weight	Composition							
	1	2	3	4	5	6	7	8
A	5.25	5.25	5.49	5.49	5.56			5.36
B						5.56		
C							5.56	
D <sup>(a)</sup>	1.75	1.75	1.83	1.83	1.85	1.85	1.85	3.57
Vinyltrimethoxy Silane								1.79
Hypalon 40s <sup>(b)</sup>	5.46							
Pergut <sup>(c)</sup>		5.46	1.17					
Xylene <sup>(d)</sup>	72.83	72.83	76.14					
Isopropanol <sup>(d)</sup>	14.71	14.71	15.37	91.58				
Ethanol : Water <sup>(e)</sup>					92.59	92.59	92.59	89.28
Acetic Acid				1.10				
% Rubber Failure	90	100	100	85	100	98	98	98

<sup>(a)</sup> Bis(trimethoxysilylpropyl)amine; <sup>(b)</sup> Chlorosulfonated Polyethylene (DuPont<sup>TM</sup> Performance Elastomers); <sup>(c)</sup> Chlorinated Natural Rubber (Bayer MaterialScience); <sup>(d)</sup> Used as received; <sup>(e)</sup> Ethanol : water (95 : 5) adjusted to pH 4 – 5 with acetic acid

*Compositions Used in EPDM Rubber to Metal Bonding*

	<b>Composition</b>	
<b>Formulation parts % by weight</b>	<b>9</b>	<b>10</b>
Hypalon 40S <sup>(a)</sup>	7.33	7.14
Xylene <sup>(b)</sup>	66.02	64.29
Aerosil 200 <sup>(c)</sup>	1.22	1.79
Heucophos ZPA <sup>(d)</sup>	3.67	5.36
GP205 <sup>(e)</sup>	9.78	14.28
Elaztobond A250 <sup>(f)</sup>	3.67	-
D	8.31	7.14
<b>% Rubber Failure</b>	<b>100</b>	<b>100</b>

<sup>(a)</sup> Chlorosulfonated Polyethylene (DuPont Performance Elastomers); <sup>(b)</sup> Used as received; <sup>(c)</sup> Hydrophilic Fumed Silica; <sup>(d)</sup> Zinc aluminium phosphate hydrate; <sup>(e)</sup> *N,N'*-4,4'-Diphenylmethane bismaleimide; <sup>(f)</sup> Resole resin.

**Testing**

**[0078]** To assess the efficacy of the adhesive systems of the present invention in bonding rubbers to metal surfaces, a series of tests were performed according to the ASTM 429-B standard adjusted to a 45° angle. Metal substrates (2.54cm (1 inch) wide, 10.16 cm (4 inch) long panels or coupons) were coated with the adhesive and adhered to natural rubber in a vulcanisation process. The natural rubber compositions were sulfur-cured compositions as set out in the Formulation tables.

**[0079]** The metal substrates were ultrasonically cleaned in an automated aqueous alkaline cleaner, rinsed with de-ionized water and blow-dried with hot air. The substrates may also be grit-blasted using a suitable abrasive agent.

**[0080]** Before application of the adhesive, 2.54 cm (1 inch) of length and 2.54 cm wide (1 inch) on both ends of the metal coupon was masked to prevent that region being available for bonding to the rubber, leaving a central area of 2.54 cm (1 inch) in width and 5.08 cm (2 inches) in length available to bond to the rubber.

**[0081]** In the bonding operation of the present invention, the compositions are applied to metal substrates by either a dipping, spraying or brush method to ensure an even coverage, preferably after the substrate has been cleaned.

**[0082]** Drying may be carried out under ambient conditions, that is room temperature. Solvent evaporation rate can be increased by heat, forced air or both.

**[0083]** A layer of uncured rubber was then placed on each coupon and cured in a standard hydraulic vulcanisation press for a period of time specified by the rubber's cure profile. In the case of the natural rubber used in the bonding process in the present invention, the rubber was cured for 20 minutes at 150 °C under a pressure of 20–30 Tonnes, to ensure intimate contact of the surfaces being bonded and the adhesive.

**[0084]** After curing the bonded samples were aged for 24 hours at room temperature before being subjected to testing and the tear pattern noted. Each sample was tested by the 45° angle modified ASTM 429-B standard using Instron test equipment (Instron<sup>TM</sup> tester, Model No. 5500R) at a steady load rate of 50 mm per minute until separation is complete.

**[0085]** “Rubber coverage” is the percentage of rubber remaining on the bonded metal substrate after peel testing. 100% rubber failure means that the rubber completely failed with no portion of the rubber peeling away from the surface of the metal (and equates to 100% rubber failure).

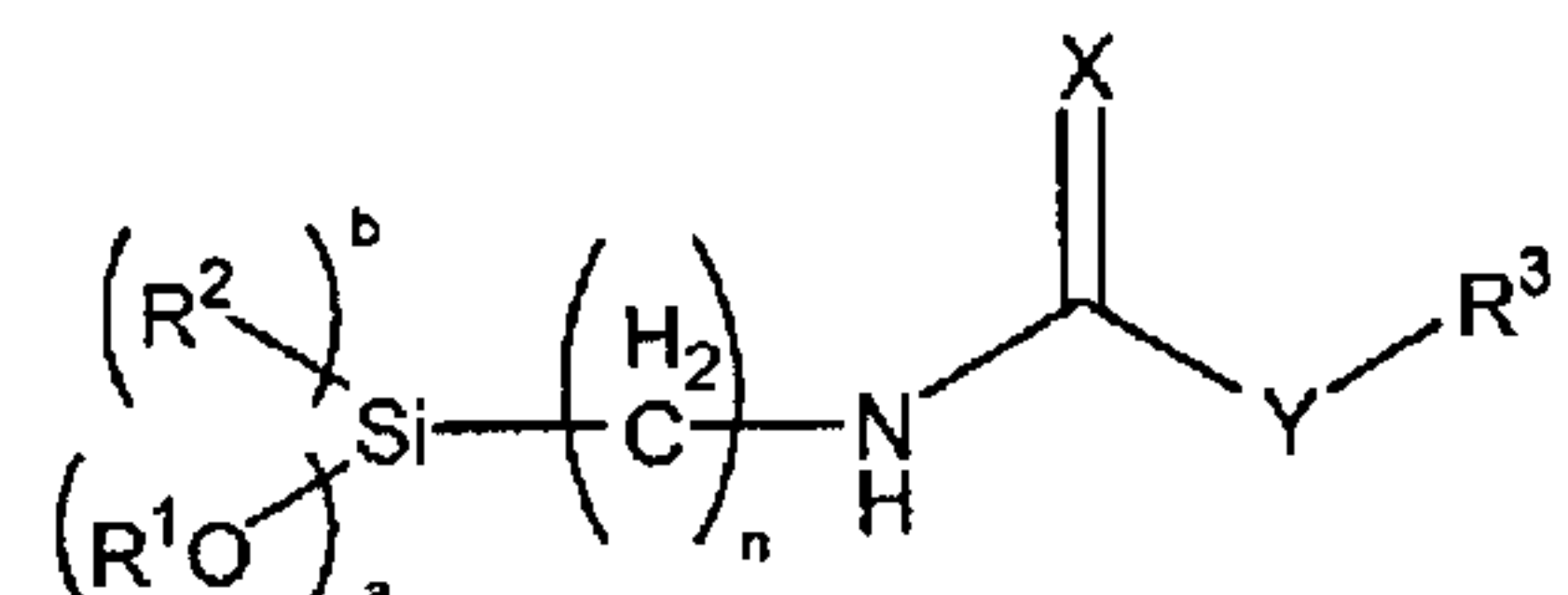
**[0086]** Generally it is desirable that the rubber substrate fails before the metal to rubber bond fails. The result is achieved with certain of the formulations as set out above.

**[0087]** The words “comprises/comprising” and the words “having/including” when used herein with reference to the present invention are used to specify the presence of stated features, integers, steps or components but do not preclude the presence or addition of one or more other features, integers, steps, components or groups thereof.

**[0088]** It is appreciated that certain features of the invention, which are, for clarity, described in the context of separate embodiments, may also be provided in combination in a single embodiment. Conversely, various features of the invention which are, for brevity, described in the context of a single embodiment, may also be provided separately or in any suitable sub-combination.

**Claims**

1. A compound of the general structure:



wherein n is 1-5;

a is 1-3 and b is 0-2; but if a = 3, b = 0; or if a = 2, b = 1; so that at least one alkoxy group is present;

R<sup>1</sup> is H, C<sub>1</sub>-C<sub>24</sub> alkyl, or C<sub>3</sub>-C<sub>24</sub> acyl, and wherein when a ≥ 1 at least one R<sup>1</sup> is not hydrogen;

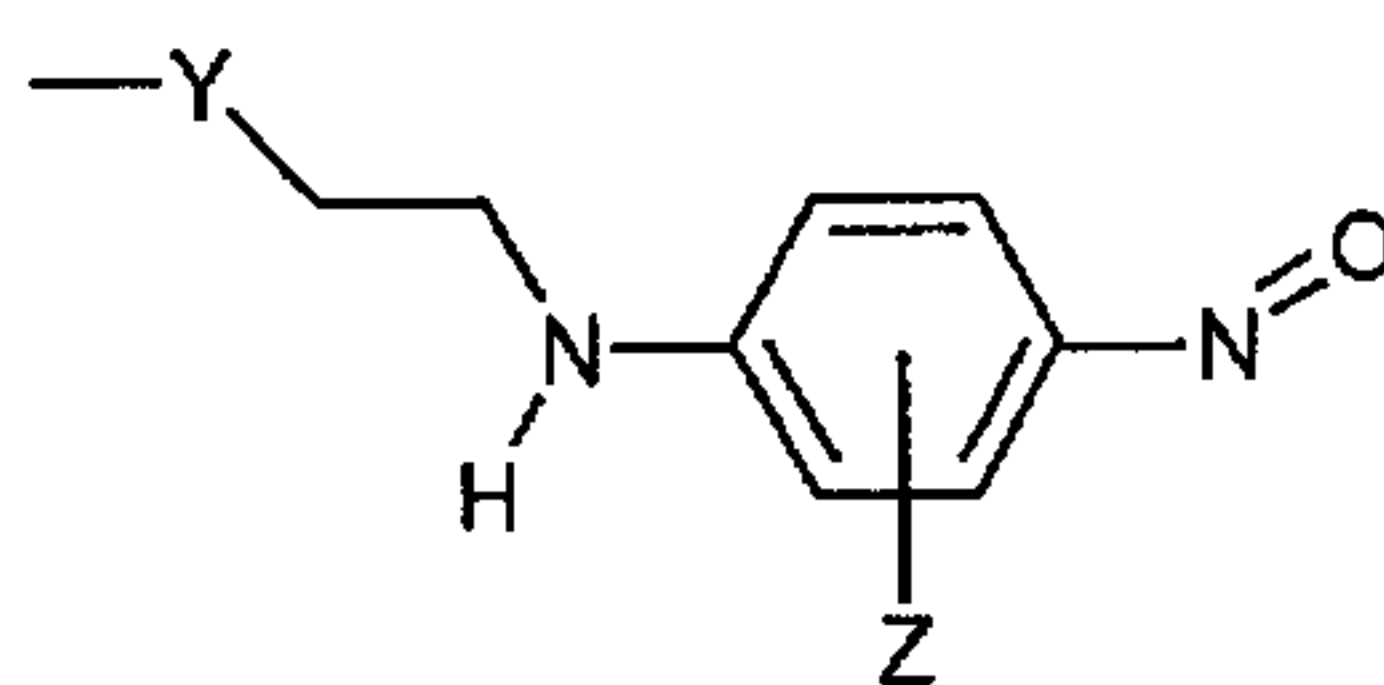
R<sup>2</sup> is C<sub>1</sub>-C<sub>24</sub> alkyl or C<sub>3</sub>-C<sub>24</sub> acyl;

X is O or S;

Y is -O, -S, or -N(R<sup>3</sup>); and

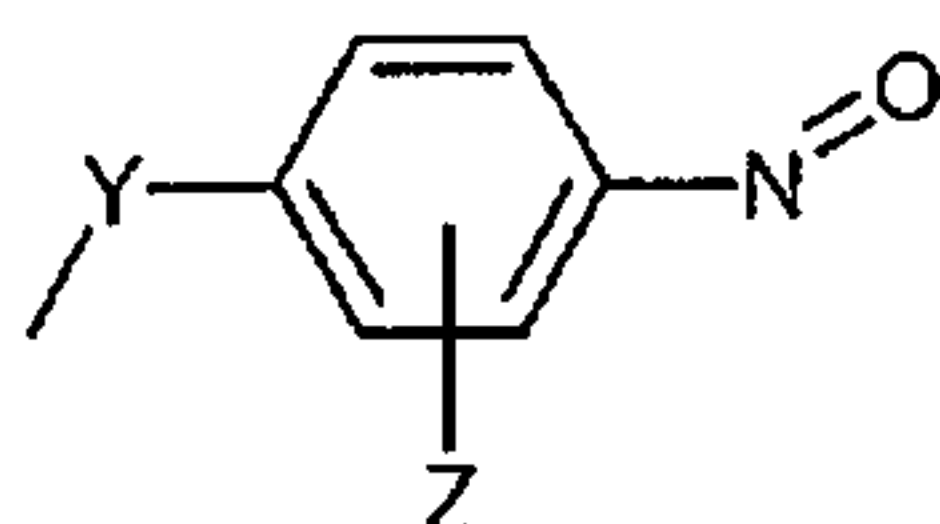
R<sup>3</sup> is a moiety comprising nitrosobenzene, quinone dioxime or quinone oxime.

2. A compound according to claim 1 wherein R<sup>3</sup> is, showing linkage through Y:



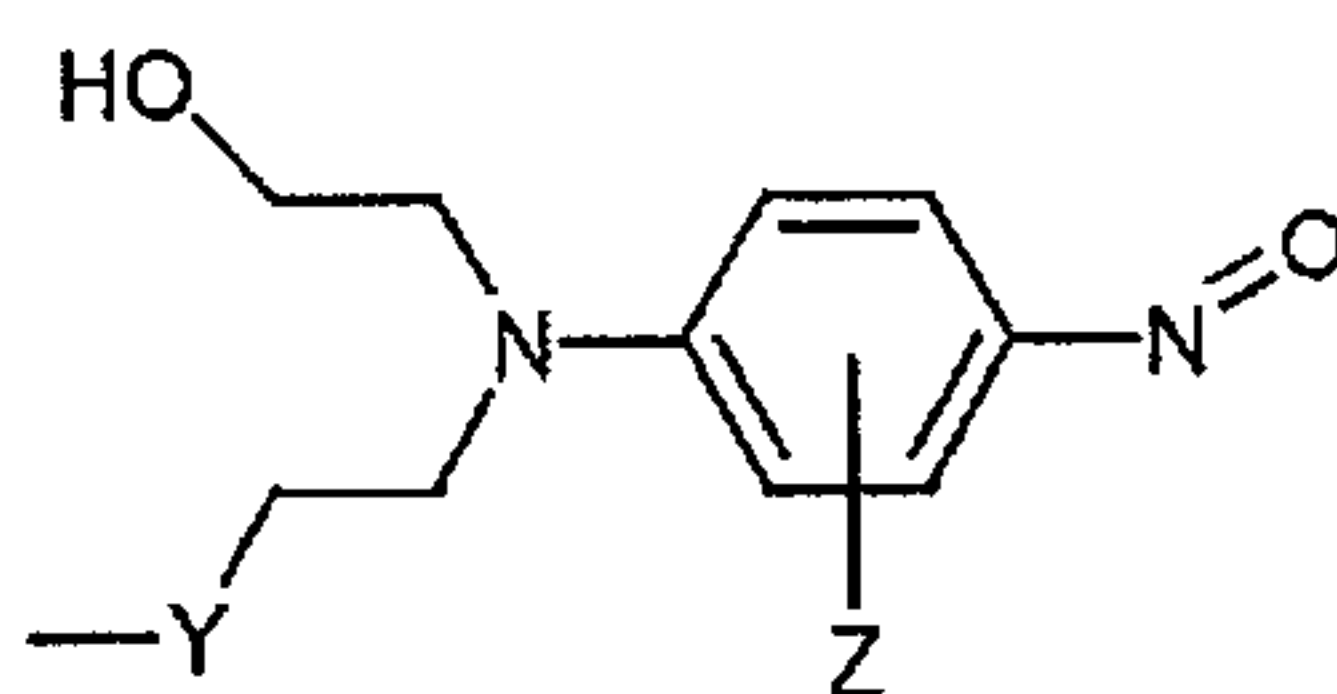
wherein Z indicates that the ring of the above structure can optionally be mono-, di-, tri- or tetrasubstituted with a group consisting of alkyl, cycloalkyl, alkoxy, aralkyl, alkaryl, arylamine, arylnitroso, amino, halogen and combinations thereof, and further wherein the substituents can either be the same or different on each carbon atom of the ring.

3. A compound according to claim 1 wherein  $R^3$  is, showing linkage through Y:



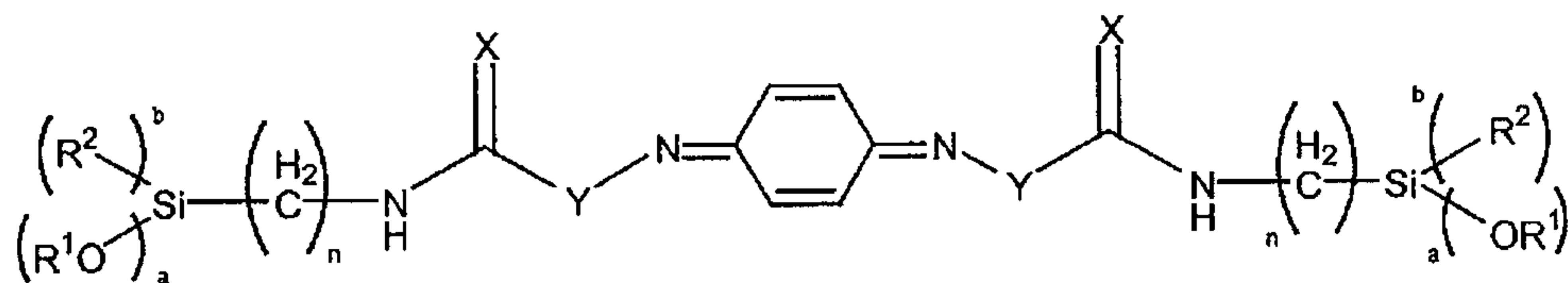
wherein Z indicates that the ring of the above structure can optionally be mono-, di-, tri- or tetrasubstituted with a group consisting of alkyl, cycloalkyl, alkoxy, aralkyl, alkaryl, arylamine, arylnitroso, amino, halogen and combinations thereof, and further wherein the substituents can either be the same or different on each carbon atom of the ring.

4. A compound according to claim 1 wherein  $R^3$  is, showing linkage through Y:



wherein Z indicates that the ring of the above structure can optionally be mono-, di-, tri- or tetrasubstituted with a group consisting of alkyl, cycloalkyl, alkoxy, aralkyl, alkaryl, arylamine, arylnitroso, amino, halogen and combinations thereof, and further wherein the substituents can either be the same or different on each carbon atom of the ring.

5. A compound of the general structure:



wherein n is 1-5;

a is 1-3 and b is 0-2; but if a = 3, b = 0; or if a = 2, b = 1; so that at least one alkoxy group is present;

$R^1$  is H,  $C_1$ - $C_{24}$  alkyl, or  $C_3$ - $C_{24}$  acyl, and wherein when  $a \geq 1$  at least one  $R^1$  is not hydrogen;

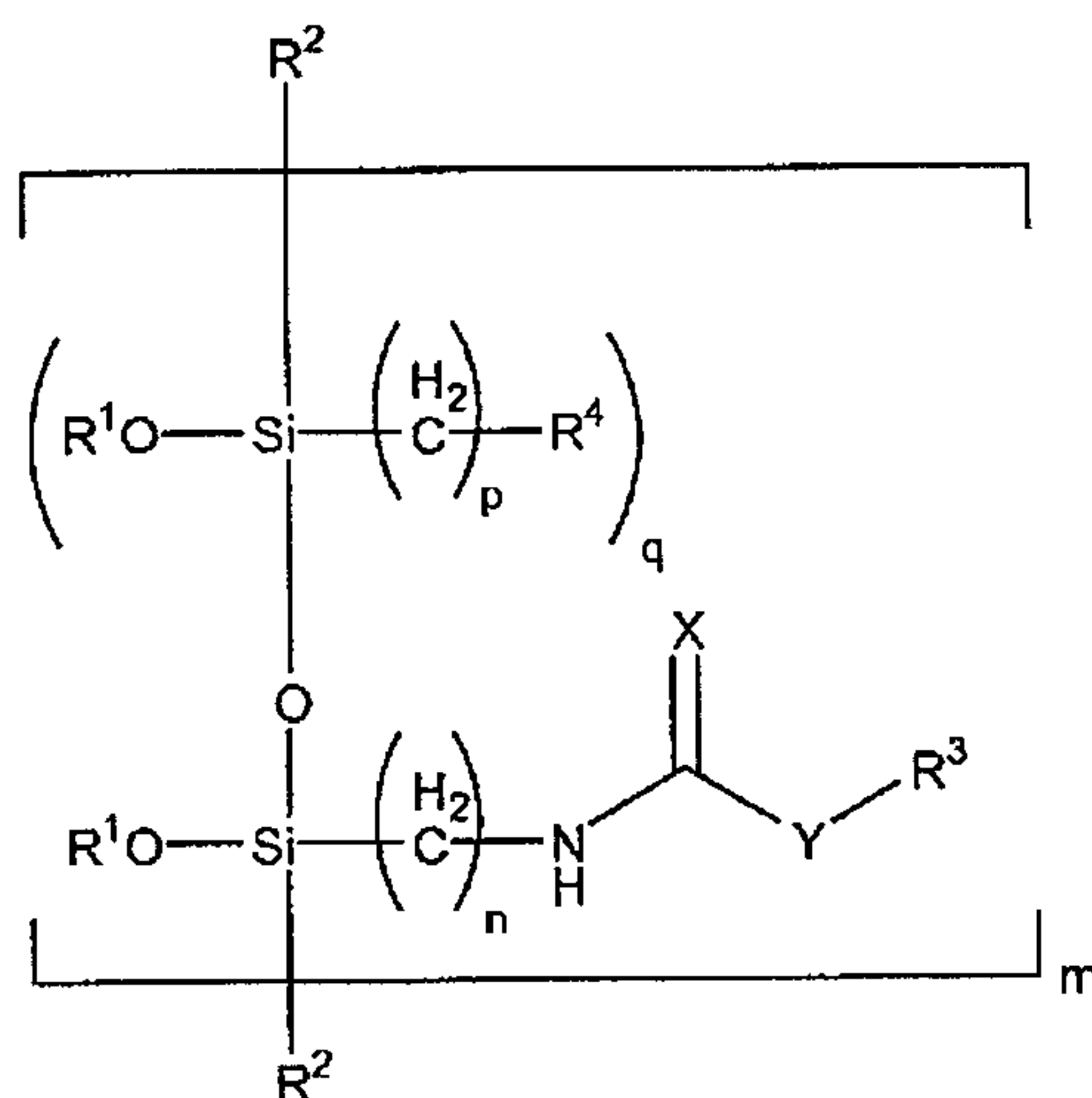
$R^2$  is  $C_1$ - $C_{24}$  alkyl or  $C_3$ - $C_{24}$  acyl;

X is O or S; and

Y is -O, -S, or  $-NH_x$ , wherein  $x = 1$  or  $2$ .

6. An oligomer or a co-oligomer of a compound according to claim 1 or 5.

7. An oligomer or a co-oligomer of a compound as defined in claim 1 which has the general structural formula:



wherein  $m$  is 1-100;  $n$  is 1-5;  $p$  is 1-5;  $q$  is 0-50; and if  $q = 0$ ,  $m \geq 2$ ;

$R^1$  is H,  $C_1$ - $C_{24}$  alkyl, or  $C_3$ - $C_{24}$  acyl;

$R^2$  is  $OR^1$ ,  $C_1$ - $C_{24}$  alkyl or  $C_3$ - $C_{24}$  acyl, and wherein when  $R^2 = OR^1$  at least one  $R^1$  is not hydrogen;

$R^4$  is acrylate, aldehyde, amino, anhydride, azide, maleimide, carboxylate, sulphonate, epoxide, ester functional, halogens, hydroxyl, isocyanate, blocked isocyanate, sulphur functional, vinyl or olefin functional, or polymeric structures;

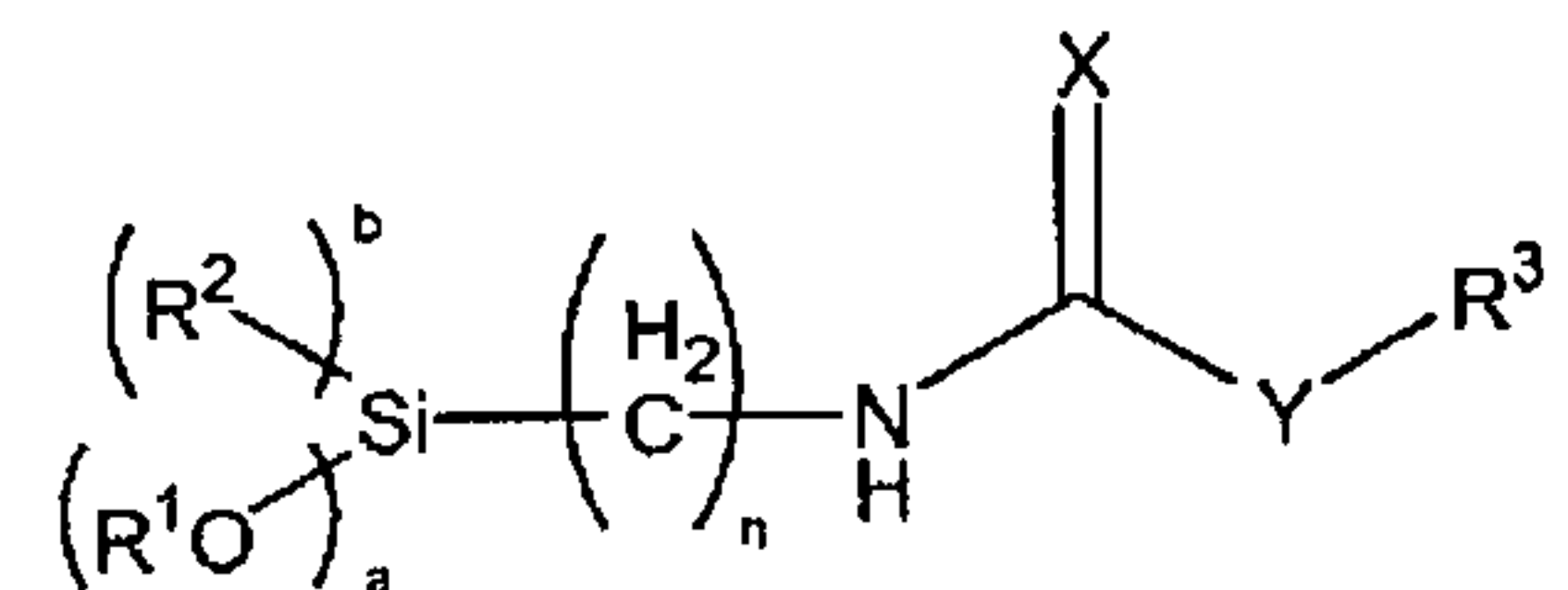
X is O or S;

Y is -O, -S, or  $-NH_x$ , where  $x = 1$  or  $2$ ; and

$R^3$  is a moiety comprising nitrosobenzene, quinone dioxime or quinone oxime.

8. A composition for bonding substrates together comprising:

i) at least one compound of the general structure:



wherein n is 1-5;

a is 1-3 and b is 0-2; but if a=3, b=0; or if a=2, b=1; so that at least one alkoxy group is present;

R<sup>1</sup> is H, C<sub>1</sub>-C<sub>24</sub> alkyl or C<sub>3</sub>-C<sub>24</sub> acyl, and wherein when a ≥ 1 at least one R<sup>1</sup> is not hydrogen;

R<sup>2</sup> is C<sub>1</sub>-C<sub>24</sub> alkyl or C<sub>3</sub>-C<sub>24</sub> acyl;

X is O or S;

Y is -O, -S, or -N(R<sup>3</sup>); and

R<sup>3</sup> is a moiety comprising nitrosobenzene, quinone dioxime or quinone oxime;

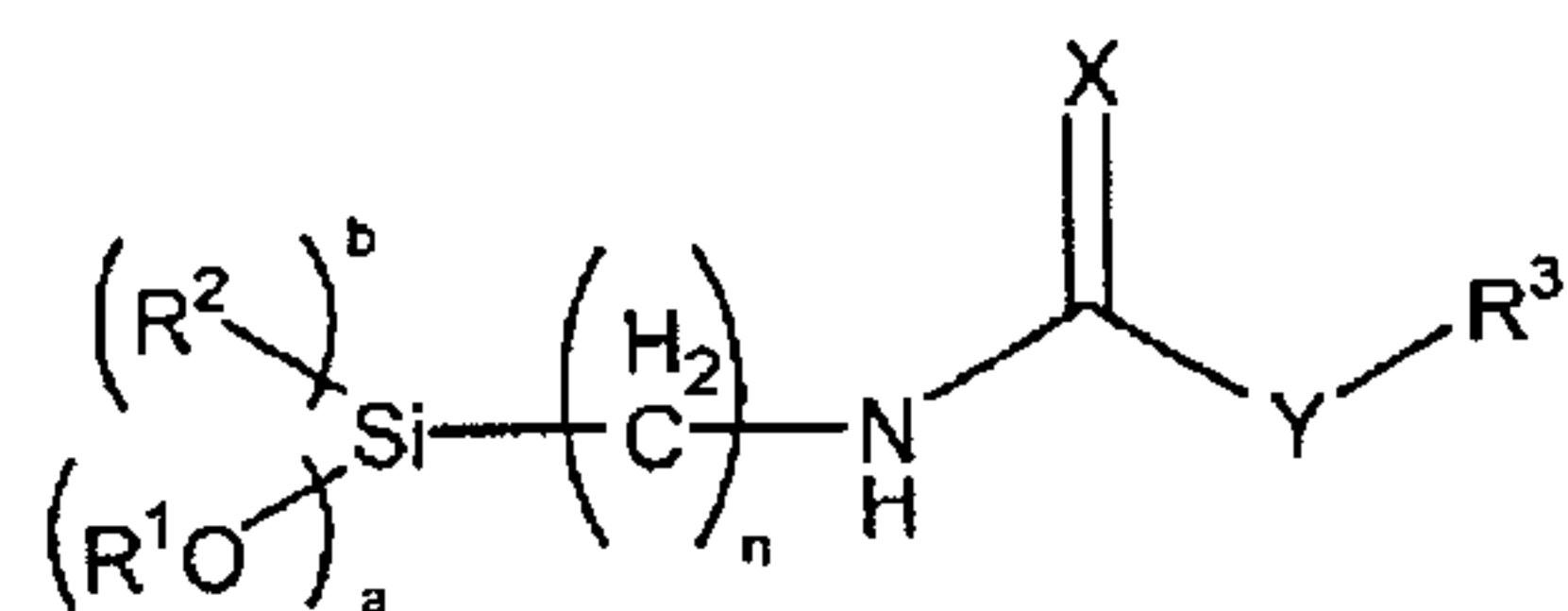
and;

ii) a carrier vehicle for the compound.

9. A process for bonding two substrates together comprising:

applying a composition comprising:

i) at least one compound of the general structure:



wherein n is 1-5;

a is 1-3 and b is 0-2; but if a=3, b=0; or if a=2, b=1; so that at least one alkoxy group is present;

R<sup>1</sup> is H, C<sub>1</sub>-C<sub>24</sub> alkyl or C<sub>3</sub>-C<sub>24</sub> acyl, and wherein when a ≥ 1 at least one R<sup>1</sup> is not hydrogen;

R<sup>2</sup> is C<sub>1</sub>-C<sub>24</sub> alkyl or C<sub>3</sub>-C<sub>24</sub> acyl;

X is O or S;

Y is -O, -S, or -N(R<sup>3</sup>); and

R<sup>3</sup> is a moiety comprising nitrosobenzene, quinone dioxime or quinone oxime;

and

ii) a carrier vehicle for the compound;

to at least one of the substrates and bringing the substrates together.

10. A process according to claim 9 wherein a first substrate comprises a natural or synthetic rubber to be bonded to a second substrate.

11. A process according to claim 10 wherein the natural or synthetic rubber substrate is vulcanised/crosslinked prior to bonding to the second substrate.

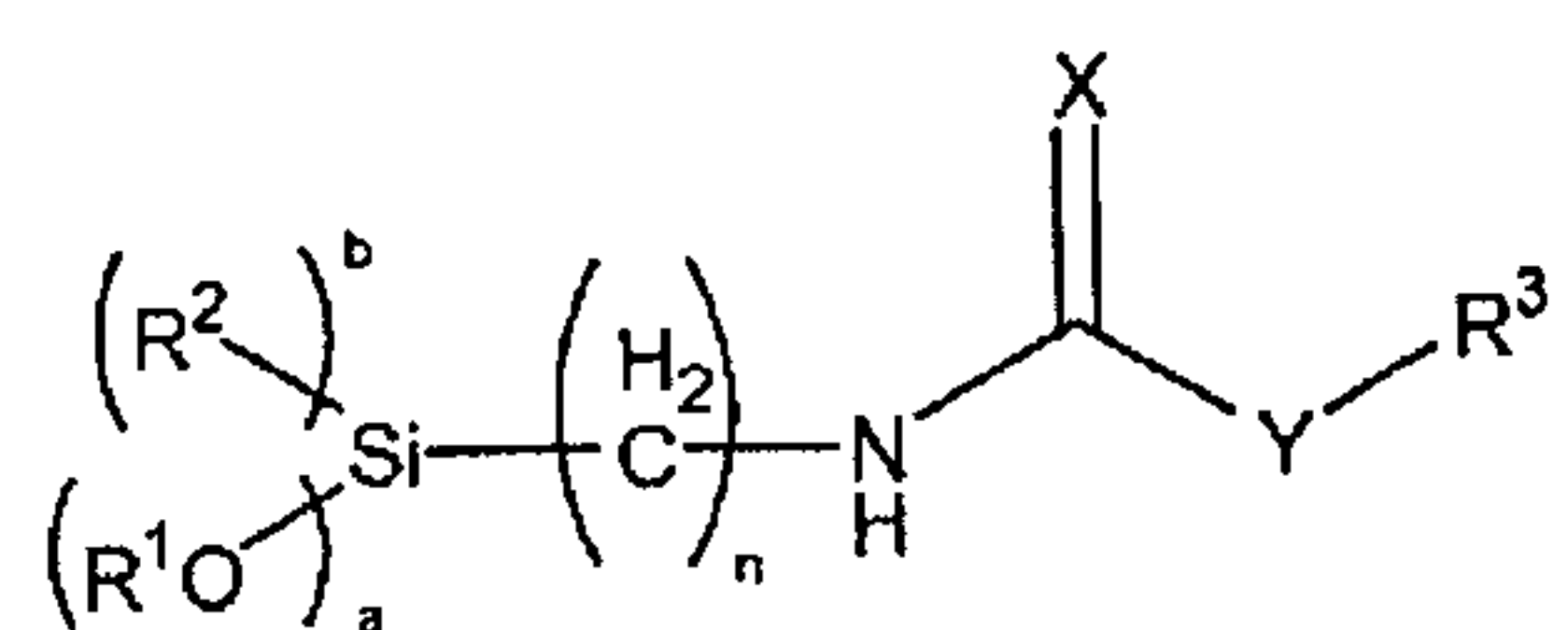
12. A process according to claim 10 wherein the natural or synthetic rubber is vulcanised/crosslinked concurrently with bonding to the second substrate.

13. A process according to claim 9 wherein a first substrate comprises a natural or synthetic rubber to be bonded to a second substrate and the second substrate is a metallic substrate.

14. A process according to claim 9 wherein said moiety selected from a nitrosobenzene, quinone dioxime or quinone oxime becomes anchored to at least one of the substrates.

15. A combination of at least two substrates bound together by an adhesive composition comprising:

i) at least one compound of the general structure:



wherein n is 1-5;

a is 1-3 and b is 0-2; but if a=3, b=0; or if a=2, b=1; so that at least one alkoxy group is present;

$R^1$  is H,  $C_1$ - $C_{24}$  alkyl or  $C_3$ - $C_{24}$  acyl, and wherein when  $a \geq 1$  at least one  $R^1$  is not hydrogen;

$R^2$  is  $C_1$ - $C_{24}$  alkyl or  $C_3$ - $C_{24}$  acyl;

X is O or S;

Y is -O, -S, or -N( $R^3$ ); and

$R^3$  is a moiety comprising nitrosobenzene, quinone dioxime or quinone oxime;

and

ii) a carrier vehicle for the compound.