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(54) Title: HYDROSILATION REACTION (57) Abstract Numerous patents teach the use of various complexes of cobalt, rhodium, nickel, palladium, or platinum as catalysts for accelerating the thermally-activated addition reaction (hydrosilation) between a compound containing silicon-bonded hydrogen and a compound containing aliphatic unsaturation. Although platinum complexes and many others are useful as catalysts in processes for accelerating the thermally-activated addition reaction between the compounds containing silicon-bonded hydrogen and compounds containing aliphatic unsaturation, processes for promoting the ultraviolet or visible radiation-activated addition reaction between these compounds are much less common. This invention provides a process for the addition reaction of compounds containing silicon-bonded hydrogen to compounds containing aliphatic unsaturation and compositions suitable for said process. The process is activated by actinic radiation and is conducted in the presence of a platinum complex having one cyclopentadienyl group that is <i>eta</i>-bonded to the platinum atom and three aliphatic groups that are <i>sigma</i>-bonded to the platinum atom and a free-radical photoinitiator that is capable of absorbing actinic radiation such that the hydrosilation reaction is initiated upon exposure to actinic radiation. The invention also provides compositions for use in the aforementioned process.		

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HYDROSILATION REACTION

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Background of the Invention

1. Field of the Invention

This invention relates to a hydrosilation
10 process involving the reaction of a compound containing
silicon-bonded hydrogen with a compound containing
aliphatic unsaturation in the presence of ultraviolet or
visible radiation, and to compositions that are useful
in that process. The invention further relates to
15 polysiloxane compositions, prepared by that process,
which compositions are useful for preparing dental
impressions, adhesives, release liners, and caulking
materials.

2. Discussion of the Art

Numerous patents teach the use of various
complexes of cobalt, rhodium, nickel, palladium, or
platinum as catalysts for accelerating the
thermally-activated addition reaction (hydrosilation)
25 between a compound containing silicon-bonded hydrogen
and a compound containing aliphatic unsaturation. For
example, U.S. Patent No. 4,288,345 (Ashby et al)
discloses as a catalyst for hydrosilation reactions a
platinum-siloxane complex. U.S. Patent No. 3,470,225
30 (Knorre et al) discloses production of organic silicon
compounds by addition of a compound containing
silicon-bonded hydrogen to organic compounds containing
at least one non-aromatic double or triple
carbon-to-carbon bond using a platinum compound of the
35 empirical formula $PtX_2(RCOCR'COR'')_2$, wherein X is
halogen, R is alkyl, R' is hydrogen or alkyl, and R'' is
alkyl or alkoxy. The catalysts disclosed in the
foregoing patents are characterized by their high

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catalytic activity. Other platinum complexes for accelerating the aforementioned thermally-activated addition reaction include: a platinacyclobutane complex
5 having the formula $(PtCl_2-C_3H_6)_2$ (U.S. Patent No. 3,159,662, Ashby); a complex of a platinous salt and an olefin (U.S. Patent No. 3,178,464, Pierpoint); a platinum-containing complex prepared by reacting chloroplatinic acid with an alcohol, ether, aldehyde, or
10 mixtures thereof (U.S. Patent No. 3,220,972, Lamoreaux); a platinum compound selected from trimethylplatinum iodide and hexamethyldiplatinum (U.S. Patent No. 3,313,773, Lamoreaux); a hydrocarbyl or halohydrocarbyl nitrile-platinum (II) halide complex (U.S. Patent No.
15 3,410,886, Joy); a hexamethyl-dipyridine-diplatinum iodide (U.S. Patent No. 3,567,755, Seyfried et al); a platinum curing catalyst obtained from the reaction of chloroplatinic acid and a ketone having up to 15 carbon atoms (U.S. Patent No. 3,814,731, Nitzsche et al); a
20 platinum compound having the general formula $(R')PtX_2$, where R' is a cyclic hydrocarbon radical or substituted cyclic hydrocarbon radical having two aliphatic carbon-carbon double bonds, and X is a halogen or alkyl radical (U.S. Patent No. 4,276,252, Kreis et al);
25 platinum alkyne complexes (U.S. Patent No. 4,603,215, Chandra et al.); platinum alkenylcyclohexene complexes (U.S. Patent No. 4,699,813, Cavezzan); and a colloidal hydrosilation catalyst provided by the reaction between a silicon hydride or a siloxane hydride and a platinum
30 (0) or platinum (II) complex (U.S. Patent No. 4,705,765, Lewis). Although these platinum complexes and many others are useful as catalysts in processes for accelerating the thermally-activated addition reaction between the compounds containing silicon-bonded hydrogen
35 and compounds containing aliphatic unsaturation, processes for promoting the ultraviolet or visible radiation-activated addition reaction between these compounds are much less common. Platinum complexes that

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can be used to initiate ultraviolet radiation-activated hydrosilation reactions have been disclosed, e.g., platinum azo complexes (U.S. Patent No. 4,670,531, Eckberg); (η^4 -cyclooctadiene)diarylplatinum complexes (U.S. Patent No. 4,530,879, Drahnak); and (η^5 -cyclopentadienyl)trialkylplatinum complexes (U.S. Patent No. 4,510,094, Drahnak). Other compositions that are curable by ultraviolet radiation include those described in U.S. Patent Nos. 4,640,939 and 4,712,092 and in European Patent Application No. 0238033. However, these patents do not indicate that the platinum complexes disclosed therein would be useful for initiating a visible radiation-activated hydrosilation reaction. U.S. Patent No. 4,916,169 describes hydrosilation reactions activated by visible radiation.

Summary of the Invention

In one aspect, this invention provides an improved process for the actinic radiation-activated addition reaction of a compound containing silicon-bonded hydrogen with a compound containing aliphatic unsaturation, said addition being referred to as hydrosilation, the improvement comprising using, as a platinum hydrosilation catalyst, an (η^5 -cyclopentadienyl)tri(σ -aliphatic)platinum complex, and, as a reaction accelerator, a free-radical photoinitiator capable of absorbing actinic radiation, i.e., light having a wavelength ranging from about 200 nm to about 800 nm. The process can also employ, as a sensitizer, a compound that absorbs actinic radiation, and that is capable of transferring energy to the aforementioned platinum complex or platinum complex/free-radical photoinitiator combination, such that the hydrosilation reaction is initiated upon exposure to actinic radiation. The process is applicable both to the synthesis of low molecular weight compounds and to the curing of high molecular weight

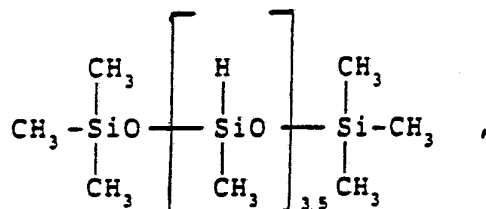
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compounds, i.e., polymers, containing unsaturated groups, e.g., $-C=C-$. For example, the process comprises exposing to actinic radiation, i.e., radiation having a wavelength of about 200 nm to about 800 nm, a composition capable of undergoing hydrosilation comprising.

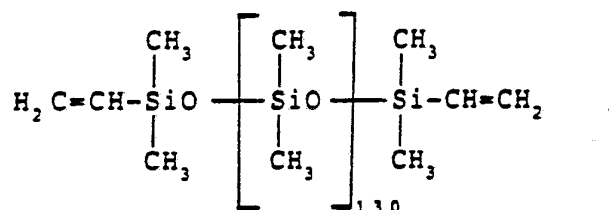
(a)

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(b)

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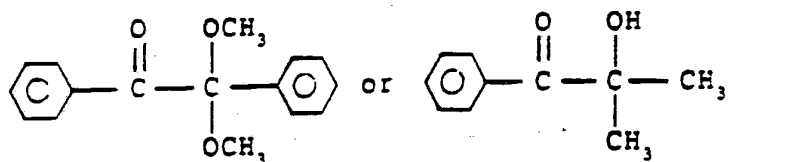
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(c) a platinum complex catalyst having one cyclopentadienyl group that is eta-bonded to the platinum atom and three aliphatic groups that are sigma-bonded to the platinum atom, and

25

(d) a free-radical photoinitiator capable of absorbing actinic radiation between 200 and 800 nm, such as:

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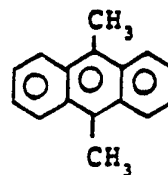
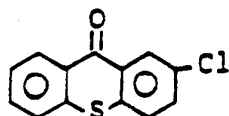
The composition can also contain a sensitizer capable of absorbing actinic radiation having a wavelength of about 200 nm to about 800 nm, such as:

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The invention further involves novel compositions, capable of undergoing hydrosilation, containing both the
10 aforementioned platinum complex and the aforementioned free-radical photoinitiator. The compositions can also contain the aforementioned sensitizer.

Important applications of the process and compositions of the invention include adhesives,
15 coatings, and light curable materials for dental applications, e.g., impressions.

The main advantage of using the free-radical photoinitiator in the actinic radiation-activated addition reaction of compounds containing silicon-bonded
20 hydrogen with compounds containing aliphatic unsaturation is the unexpectedly high acceleration of the reaction, e.g., up to about a 40% reduction in curing time.

25

Detailed Description

As used in this application, the term "compound", unless indicated otherwise, is a chemical substance which has a particular molecular identity or is made of a mixture of such substances, e.g., polymeric
30 substances. The term "hydrosilation" means the addition of organosilicon compounds containing silicon-bonded hydrogen to a compound containing an aliphatic multiple bond, and in the hydrosilation process described in this application, it refers to those processes in which
35 platinum-containing catalysts are used to effect the addition of an organosilicon compound having a silicon-bonded hydrogen atom to an aliphatically

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unsaturated compound having either olefinic or acetylenic unsaturation.

In a preferred embodiment of the invention,
5 the platinum complex is an (η^5 -cyclopentadienyl)tri(σ -aliphatic)platinum complex having the formula:



10

wherein

Cp represents a cyclopentadienyl group that is
15 eta-bonded to the platinum atom, the cyclopentadienyl group being unsubstituted or substituted with one or more groups that do not interfere in a hydrosilation reaction, and each of R^1 , R^2 , and R^3 represents an aliphatic group having from one to eighteen carbon
20 atoms, said R^1 , R^2 , and R^3 groups being sigma-bonded to the platinum atom.

The groups represented by R^1 , R^2 , and R^3 can be unsubstituted or substituted hydrocarbyl groups, or unsubstituted or substituted acyl groups, said
25 substituents, if any, not interfering in a hydrosilation reaction. The groups can be straight-chain, branched-chain, and, if sufficiently large, cyclic.

(η^5 -Cyclopentadienyl)trimethylplatinum can be prepared by the addition of a solution of
30 cyclopentadienylsodium in tetrahydrofuran to an equimolar amount of iodotrimethylplatinum dissolved in benzene, and isolation of the product complex from the reaction mixture according to the procedure of S. D. Robinson and B. L. Shaw, J. Chem. Soc., 1965, 1529.
35 Other (η^5 -cyclopentadienyl)trialiphaticplatinum complexes can be prepared by using corresponding amounts of substituted cyclopentadienylsodium in place of

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cyclopentadienylsodium and various trialiphatic platinum halides in place of iodotrimethylplatinum.

Representative examples of suitable

- 5 $(\eta^5\text{-cyclopentadienyl})$ trialiphaticplatinum complexes useful in the practice of this invention include the following, in which (Cp) represents the $(\eta^5\text{-cyclopentadienyl})$ group:

- 10 (Cp)trimethylplatinum
 (Cp)ethyldimethylplatinum
 (Cp)triethylplatinum
 (Cp)triallylplatinum
 (Cp)tripentylplatinum
 15 (Cp)trihexylplatinum
 (methyl-Cp)trimethylplatinum
 (trimethylsilyl-Cp)trimethylplatinum
 (phenyldimethylsilyl-Cp)trimethylplatinum
 (Cp)acetyldimethylplatinum

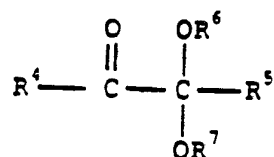
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Other suitable $(\eta^5\text{-cyclopentadienyl})$ trialiphaticplatinum complexes suitable for this invention are described in U.S. Patent No. 4,510,094, incorporated herein by reference.

- 25 Photoinitiators suitable for this invention are those compounds capable of generating free radicals upon absorption of actinic radiation between 200 and 800 nm and are preferably selected from the following classes of compounds: (1) monoketals of α -diketones or
 30 α -ketoaldehydes, and (2) acyloins and their corresponding ethers.

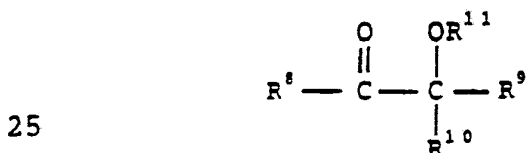
Monoketals of α -diketones and α -ketoaldehydes have the general formula:

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wherein R^4 preferably represents an aryl group that is unsubstituted or substituted with one or more groups that do not interfere with the hydrosilation reaction, and R^5 , R^6 , and R^7 each independently represents a member selected from the group consisting of an aryl group that is unsubstituted or substituted with one or more groups that do not interfere with the hydrosilation reaction, an aliphatic group having from one to eighteen carbon atoms, and hydrogen. Representative examples of these compounds are the commercially available derivatives "Irgacure" 651 (Ciba Geigy), for which R^4 and R^5 each represents the phenyl group, and R^6 and R^7 each represents the methyl group, "Irgacure" 184 (Ciba Geigy), for which R^4 represents the phenyl group, R^7 represents hydrogen, and R^5 and R^6 together represent the group $(CH_2)_5$, and "DEAP" (Union Carbide Corp.), for which R^4 represents the phenyl group, R^5 represents hydrogen, and R^6 and R^7 each represents the ethyl group.

Acyloins and their corresponding ethers have the general formula:

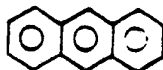


wherein R^8 preferably represents an unsubstituted aryl group or an aryl group substituted with one or more groups that do not interfere with the hydrosilation reaction, and R^9 , R^{10} , and R^{11} each independently represents a member selected from the group consisting of an aryl group that is unsubstituted or substituted with one or more groups that do not interfere with the hydrosilation reaction, an aliphatic group having from one to eighteen carbon atoms, and hydrogen. Representative examples of these compounds are the commercially available derivatives "Darocure" 1173 (EM Industries, Inc.), for which R^8 represents the phenyl

group, R^9 and R^{10} each represents the methyl group, and R^{11} represents hydrogen, "Darocure" 1116 (EM Industries, Inc.), for which R^8 represents the 4-isopropylphenyl group, R^9 and R^{10} each represents the methyl group, and R^{11} represents hydrogen, and "Vicure" 30 (Stauffer Chemical Co.), for which R^8 and R^9 each represents the phenyl group, R^{10} represents hydrogen, and R^{11} represents the methyl group.

Sensitizers suitable for this invention are those compounds capable of absorbing actinic radiation within the ultraviolet and visible regions of the electromagnetic spectrum, i.e., about 200 nm to about 800 nm, and capable of transferring energy to the platinum complex. They must not inhibit the hydrosilation reaction. Sensitizers are preferably selected from two classes of compounds: 1) polycyclic aromatic compounds, and 2) aromatic compounds containing a ketone chromophore. The sensitizer compounds can be substituted with any substituent that does not interfere with the light absorbing and energy transferring capabilities of the sensitizer compound or the hydrosilation catalyst. Examples of typical substituents include alkyl, alkoxy, aryl, aryloxy, aralkyl, alkaryl, halogen, etc. Representative examples of polycyclic aromatic sensitizers suitable for the invention include anthracene, 9-vinyanthracene, 9,10-dimethylantracene, 9,10-dichloroanthracene, 9,10-dibromoanthracene, 9,10-diethylantracene, 9,10-diethoxyanthracene, 2-ethyl-9,10-dimethylantracene, naphthacene, pentacene, benz[a]anthracene, 7,12-dimethylbenz[a]anthracene, azulene, and the like.

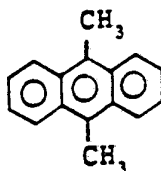
Some of the foregoing examples are illustrated below:



anthracene

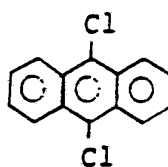
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9,10-dimethylantracene

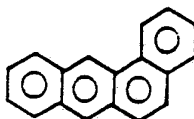
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9,10-dichloroanthracene

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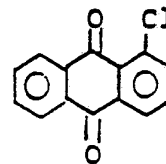
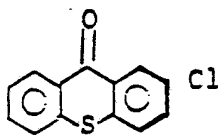
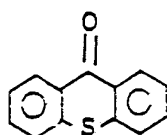


benz[a]anthracene

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Representative examples of aromatic ketone sensitizers suitable for this invention include 2-chlorothioxanthone, 2-isopropylthioxanthone, thioxanthone, anthraquinone, benzophenone, 1-chloroanthraquinone, bianthrone, and the like. Some of the foregoing examples are illustrated below:

30



35

thioxanthone 2-chlorothioxanthone 1-chloroanthraquinone

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Turning now to the reactants to be used in the radiation-activated addition reaction, compounds containing aliphatic unsaturation which are useful in the present invention have olefinic or acetylenic unsaturation. These compounds are well-known in the art of hydrosilation and are disclosed in such patents as U.S. Patent No. 3,159,662 (Ashby), U.S. Patent No. 3,220,972 (Lamoreaux), and U.S. Patent No. 3,410,886 (Joy), which disclosures of said compounds are incorporated herein. In instances where these unsaturated compounds contain elements other than carbon and hydrogen, it is preferred that these elements be either oxygen, nitrogen, silicon, a halogen, or a combination thereof. The aliphatically unsaturated compound can contain one or more carbon-to-carbon multiple bonds. Representative examples of the aliphatically unsaturated hydrocarbons which can be employed include mono-olefins, for example, ethylene, propylene, and 2-pentene; diolefins, for example, divinylbenzene, butadiene, and 1,5-hexadiene; cycloolefins, for example, cyclohexene and cycloheptene; and monoalkynes, for example, acetylene, propyne, and 1-buten-3-yne. The aliphatically unsaturated compounds can have up to 20 to 30 carbon atoms, or more.

Oxygen-containing aliphatically unsaturated compounds can also be used, especially where the unsaturation is ethylenic, such as methyl vinyl ether, divinyl ether, phenyl vinyl ether, monoallyl ether of ethylene glycol, allyl aldehyde, methyl vinyl ketone, phenyl vinyl ketone, acrylic acid, methacrylic acid, methyl acrylate, allyl acrylate, methyl methacrylate, allyl methacrylate, vinylacetic acid, vinyl acetate, and linolenic acid. Heterocyclic compounds containing aliphatic unsaturation in the ring, such as dihydrofuran, and dihydropyran, are also suitable for the present invention.

Halogenated derivatives of the previously mentioned aliphatically unsaturated compounds can be employed, including acyl chlorides as well as compounds containing a halogen substituent on a carbon atom other than a carbonyl carbon atom. Such halogen-containing compounds include, for example, vinyl chloride, and the vinyl chlorophenyl esters.

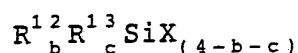
Unsaturated compounds containing nitrogen substituents such as acrylonitrile, N-vinylpyrrolidone alkyl cyanide, nitroethylene, etc., are also useful in the practice of the present invention.

Other unsaturated compounds useful in the practice of the present invention include polymers containing aliphatic unsaturation, such as the polyester resins prepared from polybasic saturated or unsaturated acids with polyhydric unsaturated alcohols, and the polyester resins prepared by reacting unsaturated polybasic acids with saturated polyhydric alcohols.

A particularly useful type of unsaturated compound which can be employed in the practice of the present invention is that containing silicon, such as those compounds commonly referred to as organosilicon monomers or polymers. These unsaturated organosilicon compounds have at least one aliphatically unsaturated organic radical attached to silicon per molecule. The aliphatically unsaturated organosilicon compounds include silanes, polysilanes, siloxanes, silazanes, as well as monomeric or polymeric materials containing silicon atoms joined together by methylene or polymethylene groups or by phenylene groups.

Preferred among the aliphatically unsaturated organosilicon compounds useful in the present invention are the monomeric silanes having the empirical formula

35



II

the cyclopolysiloxanes having the empirical formula

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5 and the polyorganosiloxanes having the empirical formula



wherein

- 10 R^{12} represents a monovalent aliphatic unsaturated hydrocarbyl group,
 R^{13} represents a monovalent saturated hydrocarbyl group,
 x represents a hydrolyzable group,
 15 b represents an integer from 1 to 4, inclusive,
 c represents zero or an integer from 1 to 3, inclusive, the
 sum of b and c being 1 to 4,
 d represents an integer from 3 to 18, inclusive,
 20 e represents a number having a value of 0.0001 to 1, inclusive, and
 f represents zero or a number such that the sum of e and f is equal to 1 to 2, inclusive.

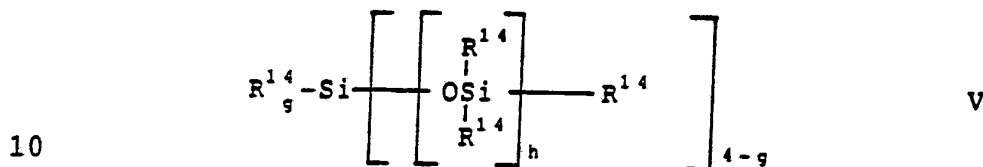
Monovalent aliphatic unsaturated hydrocarbyl
 25 groups represented by R^{12} include alkenyl, for example, vinyl, propenyl, isopropenyl, 3-butenyl, and 5-hexenyl. Groups represented by R^{13} include, for example, alkyl groups, such as methyl, ethyl, and pentyl; cycloalkyl groups, such as cyclopentyl and cyclohexyl; aryl groups
 30 such as phenyl and tolyl; aralkyl groups, such as benzyl and phenylethyl; and halogenated hydrocarbyl groups, such as haloalkyl, e.g., chloromethyl, trichloromethyl, and 3,3,3-trifluoropropyl, and haloaryl, e.g., chlorophenyl. Hydrolyzable groups represented by x
 35 include, for example, halogen groups such as chloro, bromo, and iodo; alkoxy groups such as methoxy, ethoxy, and phenoxy; and acyloxy groups such as acetoxy, propionoxy, and benzoyloxy. A hydrolyzable group is one

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which undergoes a displacement reaction with water.

In one particularly preferred embodiment of the process of the invention, the compound containing
5 aliphatic unsaturation is an aliphatically unsaturated polyorganosiloxane represented by the general formula:



wherein

each R^{14} can be the same or different and represents a non-halogenated or halogenated
15 ethylenically-unsaturated group having from 2 to 18 carbon atoms, such as vinyl, propenyl, and chlorovinyl, a non-halogenated or halogenated alkyl group having from 1 to 18 carbon atoms, such as methyl, ethyl, propyl,
20 hexyl, octyl, dodecyl, octadecyl, trichloromethyl, and 3,3,3-trifluoropropyl, a non-halogenated or halogenated cycloalkyl group having from 3 to 12 carbon atoms, such as cyclopentyl and cyclohexyl, or phenyl, at
25 least 70% of all R^{14} groups being methyl groups, but no more than 10% of all R^{14} groups being vinyl or other alkenyl, e.g., having 3 to 18 carbon atoms, and at least one of the R^{14} groups being vinyl or other alkenyl, e.g.,
30. having 3 to 18 carbon atoms;
h represents a number having a value from 1 to about 3,000; and
g represents 0, 1, 2, or 3.

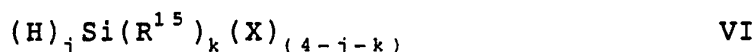
The reactant containing the silicon-hydrogen
35 linkage can be a polymeric compound or a compound that is not polymeric. These compounds are well-known in the art and are disclosed in the patents which describe the aliphatically unsaturated reactant, i.e., Ashby, U.S.

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Patent No. 3,159,662; Lamoreaux, U.S. Patent No. 3,220,972; and Joy, U.S. Patent No. 3,410,886. The reactant containing the silicon-hydrogen linkage should
 5 contain at least one silicon-bonded hydrogen atom per molecule, with no more than three hydrogen atoms attached to any one silicon atom.

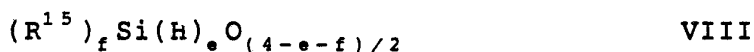
Some classes of compounds having a silicon-bonded hydrogen atom which can be used in the
 10 invention are organosilanes having the empirical formula:



15 organocyclopolysiloxanes having the empirical formula:



and organohydrosiloxane polymers or copolymers having
 20 the empirical formula:



wherein

- 25 R^{15} represents an organic group, preferably selected from the group consisting of monovalent hydrocarbyl groups, and halogenated monovalent hydrocarbyl groups,
 j represents the integer 1, 2, or 3,
 30 k represents zero or an integer of 1 to 3, inclusive, the sum of j and k being equal to 1 to 4, and

X, d, e and f are as defined above for formulas II, III, and IV.

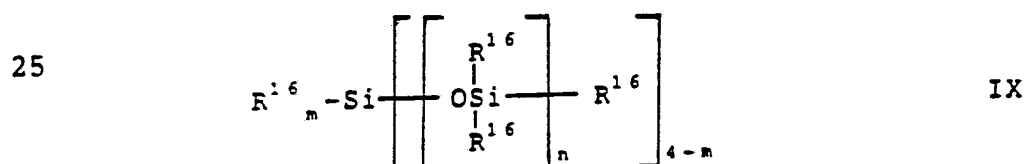
- 35 Among the groups represented by R^{15} include, for example, alkyl groups having 1 to 18 carbon atoms, e.g., methyl, ethyl, propyl, octyl, and octadecyl; cycloalkyl groups having 5 to 7 ring carbon atoms, e.g.,

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cyclohexyl and cycloheptyl; aryl groups having 6 to 18 carbon atoms, e.g., phenyl, naphthyl, tolyl, xylyl; and combinations of alkyl and aryl groups, e.g., aralkyl groups, such as, benzyl and phenylethyl, and halo-substituted groups thereof, e.g., chloromethyl, chlorophenyl, and dibromophenyl. Preferably, the R^{15} group is methyl or both methyl and phenyl. The R^{15} group can also be an unsaturated aliphatic group having 1 to 20 carbon atoms, such as alkenyl or cycloalkenyl, e.g., vinyl, allyl and cyclohexenyl. When the R^{15} group is a group with aliphatic unsaturation, the silicon compound containing silicon-hydrogen linkages can be reacted with itself to form a polymer.

Among the inorganic compounds which contain silicon-bonded hydrogen atoms and which are useful as reactants in the process of the present invention are included, for example, trichlorosilane, dibromosilane, pentachlorodisilane, pentachlorodisiloxane, and heptachlorotrisilane.

A preferred compound having silicon-bonded hydrogen useful in this invention is a polyorganohydrosiloxane having the general formula:



wherein

- each R^{16} can be the same or different and represents hydrogen, an alkyl group having 1 to 18 carbon atoms, a cycloalkyl group having 3 to 12 carbon atoms, or a phenyl group, at least one but not more than one-half of all the R^{16} groups in the siloxane being hydrogen,
- m represents 0, 1, 2, or 3, and
- n represents a number having an average value from 1 to about 3,000.

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The hydrosilation composition useful in the synthesis of low molecular weight compounds by the process of the invention can be prepared by mixing about 5 0.1 to about 10.0 equivalent weights of the compound having silicon-bonded hydrogen with one equivalent weight of the compound having aliphatic unsaturation and then adding an amount of platinum complex catalyst sufficient to catalyze the reaction and an amount of a 10 free-radical photoinitiator sufficient to accelerate the reaction. Optionally, an amount of a sensitizer sufficient to sensitize the platinum complex/free-radical photoinitiator combination upon exposure to actinic radiation having a wavelength from 15 about 200 nm to about 800 nm can also be added. The amount of the catalyst can range from about 5 to about 1,000 parts by weight, preferably from about 50 to about 500 parts by weight, per 1,000,000 parts by weight of the total composition. The amount of free-radical 20 photoinitiator can range from about 50 to about 50,000 parts by weight, preferably from about 100 to about 5,000 parts by weight, per 1,000,000 parts by weight of the total composition. The amount of sensitizer can range from about 50 to about 50,000 parts by weight, 25 preferably from about 100 to about 5,000 parts by weight, per 1,000,000 parts by weight of the total composition.

Known techniques can be used to conduct the hydrosilation reaction. In carrying out a hydrosilation 30 reaction in the practice of this invention, the reactants and catalyst can be introduced into a vessel equipped for stirring, where the mixture is stirred until it is homogenous. If either of the reactants is a solid or is extremely viscous, a solvent can be 35 introduced into the vessel to facilitate uniform mixing of the reactants. Suitable solvents include aromatic hydrocarbons, such as xylene and toluene; aliphatic hydrocarbons, such as hexane and mineral spirits; and

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halogenated hydrocarbons, such as chlorobenzene and trichloroethane. It is desirable that the solvent be transmissive to actinic radiation. From about 0.1 to
5 about 10 parts of solvent per part by weight of the combined reactants may be used. The resulting reaction product will generally be sufficiently pure for its intended use. However, it may be desirable to remove the solvent if one has been employed.

10 The hydrosilation compositions useful in the preparation of higher molecular weight cured siloxane polymers, by the process of this invention, can be prepared by mixing an aliphatically unsaturated polysiloxane and the compound having silicon-bonded
15 hydrogen in such a proportion so as to provide about 0.1 to about 10.0 silicon-bonded hydrogen atoms per unsaturated group, and then adding from about 5 to about 1,000 parts by weight, preferably from about 50 to about 500 parts by weight of platinum complex catalyst and
20 from about 50 to about 50,000 parts by weight, preferably from about 100 to about 5,000 parts by weight of a free-radical photoinitiator. Optionally, from about 50 to about 50,000 parts by weight, preferably from about 100 to about 5,000 parts by weight of
25 sensitizer, per 1,000,000 parts by weight of the total composition, can be added. The reaction mixture can be mixed, as by stirring, blending, or tumbling, until it is homogenous.

The thoroughly mixed composition can then be
30 applied to a substrate by any suitable means, such as by spraying, dipping, knife coating, curtain coating, roll coating, or the like, and the coating cured by using conventional techniques for providing actinic radiation. It is preferred that curing be conducted by exposing the
35 coated substrate to radiation having a wavelength of about 200 nm to about 800 nm. Depending on the particular silicone formulation, catalyst, free-radical photoinitiator, optional sensitizer, and intensity of

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the actinic radiation, curing can be accomplished in a period from less than one second to less than 30 minutes. Any radiation source emitting radiation above
5 about 200 nm can be used. Examples of suitable radiation sources include tungsten halogen lamps, xenon arc lamps, mercury arc lamps, incandescent lamps, and fluorescent lamps. Particularly preferred sources of actinic radiation are tungsten halogen, xenon arc, and
10 mercury arc lamps.

Various additives conventionally included in hydrosilation compositions can be included in the curable compositions, depending on the intended purpose of the composition. Fillers and/or pigments, such as
15 chopped fibers, crushed polymers, talc, clay, titanium dioxide, and fumed silica can be added. Soluble dyes, oxidation inhibitors, and/or any material that does not interfere with the catalytic activity of the platinum complex and does not absorb actinic radiation at the
20 absorption wavelength of the free-radical photoinitiator, or of the optional sensitizer, can be added to the composition.

The shelf life of the curable compositions containing the catalyst and sensitizer can be extended
25 by the addition of a conventional catalyst inhibitor. The amount of catalyst inhibitor can vary from about 1 to about 10 times, or more, the amount of platinum complex, depending on the activity of the particular complex or complex-accelerator used and the shelf life
30 desired for the composition. Greater amounts of inhibitor should be used with the more active complexes, with lesser amounts being used for the less active complexes. Hydrosilation inhibitors are well known in the art and include such compounds as acetylenic
35 alcohols, certain polyolefinic siloxanes, pyridine, acrylonitrile, organic phosphines and phosphites, unsaturated amides, and alkyl maleates.

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The hydrosilation compositions of this invention can be applied to the surface of any solid substrate for a variety of purposes. Examples of such
5 substrates include paper, cardboard, wood, cork, plastic, such as polyester, nylon, polycarbonate, etc., woven and nonwoven fabric, such as cotton, polyester, nylon, etc., metal, glass, and ceramic.

It is often advantageous to prime the surface
10 of non-porous substrates to which the hydrosilation composition is to be applied to improve the adhesion of the composition to the substrate. Many primers and priming techniques (e.g., corona treatment) are described in the art and should be chosen on the basis
15 of the substrate to be used. For example, the epoxy-functional siloxanes as taught in U.S. Patent No. 4,243,718 (Murai et al) are useful for priming the surface of plastic films such as polyester and polyvinylchloride.

20 Compositions of this invention can be applied and cured in relatively thick sections, such as an impression material for dental applications or a fast-setting caulking material.

Advantages of this invention are further
25 illustrated by the following examples, where the parts referred to are parts by weight. The particular materials and amounts recited as well as other conditions and details given should not be construed to unduly limit this invention.

30 Compositions of this inventions were evaluated for cure speed in the following manner.

Molds made from a 1.5 mm thick "Teflon" sheet with a 6 mm diameter hole through the sheet were clamped to clean glass slides so that the central axis of the
35 hole in the mold was normal to the glass slide. The hole was filled with a sample of the composition being evaluated. A "Visilux" 2 dental curing light (available from Minnesota Mining and Manufacturing Company) with a

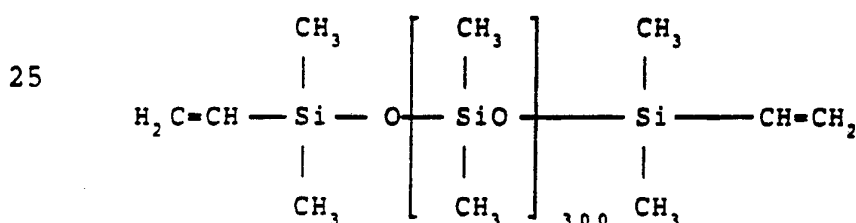
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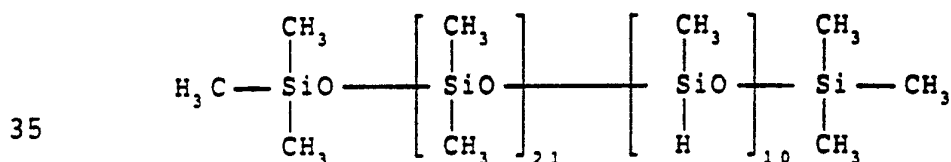
light output in the visible region of the spectrum between 400 and 500 nm was clamped to a ring stand and positioned such that the cylindrical tip of the light source was 5.0 mm above the top of the "Teflon" mold. The center of the 6 mm diameter sample was directly beneath the light tip. The sample was irradiated with the "Visilux" 2 light until a tack-free, cohesive silicone polymer was obtained as determined with a metal probe. Compositions were evaluated for cure speed under ultraviolet radiation by placing small samples of each formulation in shallow 2 inch diameter aluminum pans and irradiating the samples at a distance of 25 cm under a bank of six Sylvania 15 Watt "Black Light" bulbs or at a distance of 5 mm from a Caulk/Hanovia "Black Light", each with a maximum intensity output at 365 nm. All samples were tested in duplicate or triplicate.

Example 1

A stock composition was prepared by mixing in a glass container 85 parts by weight of vinyl terminated polydimethylsiloxane polymer having the formula:



and 15 parts by weight of a compound containing silicon-bonded hydrogen atoms having the formula:



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To 10.0 g portions of this stock composition were added the photohydrosilation catalyst $\text{CpPt}(\text{CH}_3)_3$ at a concentration of 960 ppm platinum and a photoinitiator selected from "Irgacure" 651, "Irgacure" 184, "Darocure" 1173, and "Darocure" 1116 at a concentration of 1,000 ppm. Compositions were irradiated as previously described, and the times until gelation of these compositions are set forth in Table I.

10

Table I

Photoinitiator	<u>Gel time (sec)</u>	
	Ultraviolet ("Black Light")	Visible ("Visilux"2)
---	123	162
"Irgacure" 651	118	107
"Irgacure" 184	113	116
"Darocure" 1173	111	136
"Darocure" 1116	101	108

The results in Table I indicate that several photoinitiators are capable of increasing the speed of a hydrosilation reaction.

25

Example 2

To each of four 2 g portions of the stock composition of Example 1 in glass vials were added 960 ppm platinum in the form of $\text{CpPt}(\text{CH}_3)_3$ and from 0 to 4,000 ppm of the photoinitiator "Darocure" 1173. Compositions were irradiated as previously described, and gelation times of each composition are set forth in Table II.

35

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Table II

	Amount of photoinitiator (ppm)	<u>Gel time (sec)</u>	
		Ultraviolet (Caulk/Hanovia)	Visible ("Visilux"2)
5	--	240	143
	1333	137	130
	2666	137	124
10	4000	143	118

The data in Table II show that the rate of cure increases with increasing amounts of "Darocure" 1173 photoinitiator under a source of visible light up to a level of at least 4,000 ppm and under a source of ultraviolet light to a level of approximately 1,333 ppm.

Example 3

To each of four compositions prepared as described in Example 2 were added 960 ppm platinum in the form of $\text{CpPt}(\text{CH}_3)_3$ and 1,000 ppm of the photosensitizer 2-chlorothioxanthone. Samples were irradiated as previously described, and the time until gelation of these compositions is set forth in Table III.

Table III

5	Amount of photosensitizer (ppm)	Amount of photoinitiator (ppm)	Gel time (sec)	
			Ultraviolet (Caulk/Hanovia)	Visible ("Visilux" 2)
	--	--	240	143
10	1,000	--	162	40
	1,000	1,333	164	38
	1,000	2,666	155	35
	1,000	4,000	134	25

15

The data in Table III show that the addition of 2-chlorothioxanthone results in a significant enhancement of cure speed relative to that of the unsensitized compositions. Further enhancement can be achieved upon addition of "Darocure" 1173 photoinitiator up to a level of at least 4,000 ppm under a source of either ultraviolet or visible light.

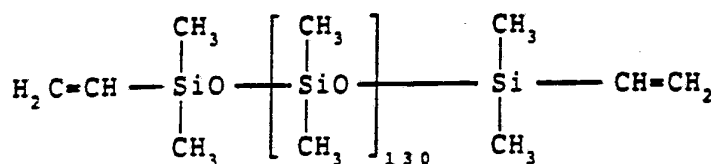
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Example 4

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A stock composition was prepared by mixing in a glass container 97.5 parts by weight of a vinyl-terminated polydimethylsiloxane having the formula:

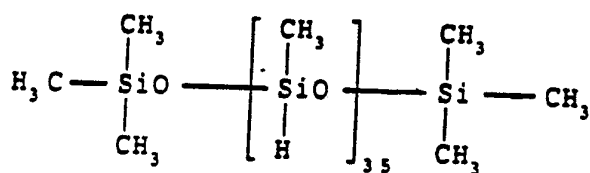
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35

and 2.5 parts by weight of a compound containing silicon-bonded hydrogen having the formula:

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5

To 10.0 g aliquots of this composition were added
 CpPt(CH₃)₃ to the extent of from 50 to 500 ppm Pt and
 varying amounts of a photoinitiator selected from
 "Irgacure" 651, "Irgacure" 184, "Darocure" 1173, and
 10 "Darocure" 1116. Samples were irradiated as previously
 described, and the time until gelation of these
 compositions is set forth in Table IV.

Table IV

15	Photo- initiator	Amount (ppm)	Amount of catalyst (ppm)	Gel time (sec)	
				Ultraviolet ("Black Light")	Visible ("Visilux"2)
20	-	-	50	130	130
	-	-	200	70	75
	-	-	500	60	60
25	"Irgacure" 651	500	50	250	> 300
		500	500	50	40
		100	200	65	69
		100	500	52	57
30	"Irgacure" 184	500	500	55	49
		100	500	53	59
	"Darocure" 1173	500	500	53	46
35		100	500	52	60
	"Darocure" 1116	500	500	50	48
		100	500	52	56

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The data in Table IV show that the greatest increase in cure speed is observed when the catalyst and photoinitiator are present in approximately equal amounts.

Example 5

This example illustrates the release characteristics of coatings prepared with the compositions of this invention. To a 30.0 g aliquot of the stock composition of Example 2 were added 9.4 mg of $\text{CpPt}(\text{CH}_3)_3$ (200 ppm Pt), 15 mg of 2-chlorothioxanthone (500 ppm), and 15 mg of "Irgacure" 651 photoinitiator (500 ppm). The composition was coated on super calendered Kraft paper at a coating weight of 1 to 2 g/m^2 and cured by irradiation under an atmosphere of nitrogen in a PPG processor that advanced the sample at a rate of 50 cm/sec under two medium pressure mercury lamps emitting 120 watts of radiation per centimeter of lamp length and subsequent heating in a circulating air oven at 100°C for 2 minutes. Similarly coated samples that were not exposed to radiation did not cure when heated at 100°C.

The release value of the cured silicone coating was determined by the following procedure: A heptane-isopropyl alcohol solution of pressure-sensitive adhesive comprising isooctyl acrylate (95.5% by weight)-acrylic acid (4.5% by weight) copolymer, as described in Example 5 of U.S. Patent No. Re. 24,906, incorporated herein by reference, was applied to the cured silicone coating and dried for 5 minutes at 70°C in a circulating air oven to give a dry coating weight of 32 g/m^2 . A biaxially oriented film of polyethylene terephthalate (PET) (38 micrometers thick) was pressed against the surface of the coating to produce a laminate consisting of a pressure-sensitive adhesive tape and a silicone-coated substrate. The laminate was cut into 2.5 x 25 cm strips. An average value of 15 g per 2.5 cm

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of width was measured to be the force required to pull the PET film with adhesive attached thereto (i.e., a pressure-sensitive adhesive tape) away from the
5 silicone-coated substrate at an angle of 180° and a pulling speed of 230 cm/min.

The readhesion value of the pressure-sensitive tapes was determined by the following procedure: The pressure-sensitive tapes, as removed from the silicone
10 coated surface, were applied to the surface of a clean glass plate. An average value of 1,400 g per 2.5 cm of width was measured to be the force required to pull the tape from the glass surface at an angle of 180° and a pulling speed of 230 cm/min. A control readhesion value
15 was obtained for the pressure-sensitive tape by applying the tape, which had not been placed in contact with a silicone-coated surface, to a clean glass plate and measuring the force required to remove the tape from the plate. The control readhesion value was 1,500 g per 2.5
20 cm of width.

Example 6

This example illustrates the preparation of a silicone-based pressure-sensitive adhesive tape from a
25 composition of this invention. A mixture of the following three ingredients was prepared:

- 30 (1) 13.6 g of a dimethylvinylsiloxyl endblocked polydimethylsiloxane containing an average of 25.1 dimethylsiloxane units per molecule;
- (2) 25.6 g of a dimethylhydrogensiloxyl endblocked polydimethylsiloxane containing an average of 28.7 dimethylsiloxane units per molecule; and
- 35 (3) 100.0 g of a 60 percent by weight solution in xylene of a resinous organosiloxane copolymer comprising $\text{CH}_3\text{SiO}_{1/2}$, $\text{SiO}_{5/2}\text{H}$ and $\text{SiO}_{4/2}$ units in a ratio of 41.6 : 10.5: 47.6. The copolymer exhibited a number average molecular

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weight, determined by gel permeation chromatography, of about 2,600 and a dispersity index of 2.6.

5

The mixture was stripped of volatile material by heating at 65°C under less than 0.5 mm of Hg pressure on a rotary evaporator. To the resulting viscous mixture were added 0.80 g of

10 1,3,5,7-tetravinyltetramethylcyclotetra-
siloxane, 2.0 g of toluene, 78 mg of $\text{CpPt}(\text{CH}_3)_3$ (500 ppm Pt), 100 mg of 2-chlorothioxanthone (1,000 ppm), and 100 mg of "Irgacure" 651 photoinitiator (1,000 ppm). The composition was knife coated at a thickness of 0.05 mm
15 on a 0.05 mm thick polyethylene terephthalate film, and the coating was cured by irradiation under an atmosphere of nitrogen in a PPG processor that advanced the sample at a rate of 50 cm/sec under two medium pressure mercury lamps emitting 120 watts of radiation per centimeter of
20 lamp length and subsequent heating in a circulating air oven at 100°C for two minutes.

Adhesion was determined essentially according to the procedure described in ASTM D-330 (1983). Strips of the tape 2.54 cm wide and approximately 25 cm long
25 were adhered to a glass surface using a 2.04 kg rolled weight. An average value of 1,600 g per 2.5 cm of width was measured to be the force required to pull the adhesive tape away from the glass surface at an angle of 180° and a pulling speed of 230 cm/min.

30 Shear strength was determined essentially according to the procedure described in ASTM D-3654 (1982). Specimens 1.27 cm wide and approximately 8 cm long were adhered to a bright annealed steel surface with an overlap area of 1.27 cm by 1.27 cm. The samples
35 were suspended vertically and maintained at a temperature of 70°C for one hour. A 1 kg weight was suspended from the free end of each specimen, and an average of 200 minutes was measured as the elapsed time

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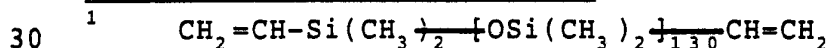
before the adhesive bond failed while being maintained at a temperature of 70°C. The test was repeated at room temperature, and an average holding time exceeding 10,000 minutes was measured.

The tack of the adhesive tape was measured qualitatively by touching the cured adhesive with a finger. Tack was judged to be moderate.

10 Example 7

This example illustrates the preparation of a conformal coating for electronic components using a composition of this invention. A composition consisting of the following ingredients in the amounts indicated was prepared:

<u>Ingredient</u>	<u>Amount (parts by weight)</u>
Vinyl siloxane polymer ¹	54.2
Crosslinking Agent	
20 (PMC 54, available from Minnesota Mining and Manufacturing Company)	30.8
Catalyst (CpPt(CH ₃) ₃)	0.031
Sensitizer (2-chlorothioxanthone)	0.050
25 Photoinitiator ("Irgacure" 651)	0.050
Fumed silica	
("Quso", available from Degussa Corporation)	15.0



The ingredients were introduced into a 250 ml beaker and mixed thoroughly. The mixture was transferred to a 50 cc syringe and degassed under reduced pressure for approximately 30 minutes to yield a bubble-free mixture.

The composition was applied to an integrated circuit board measuring 2 inches by 2 inches in

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sufficient quantity to provide a coating approximately 1 mm in thickness. The coating was irradiated with a "Visilux" 2 light source for approximately 4 minutes to provide a tough, elastomeric, transparent coating that adhered well to the circuit board.

Example 8

This example illustrates preparation of a dental impression by means of a visible-light curable wash material and a chemically curable tray material.

A polyvinylsiloxane formulation curable by visible light was prepared by mixing the following ingredients in the amounts indicated:

Indegredient	<u>Amount</u>	
	(g)	(wt %)
Vinyl-terminated polysiloxane		
polymer of Example 1	8.5	76.81
20 Crosslinking agent of Example 1	1.5	13.56
Catalyst ($\text{CpPt}(\text{CH}_3)_3$)	0.015	0.14
Sensitizer (2-chlorothioxanthone)	0.01	0.09
Photoinitiator ("Darocure" 1173)	0.04	0.36
Fumed Silica ("Aerosol" R-972,		
25 available from Degussa)	<u>1.0</u>	<u>9.04</u>
	11.065	100.00

The first four ingredients were premixed; then fumed silica was added. The resultant mixture was painted on the entire surface of a single tooth of a typodont. The coated surface was then irradiated by means of a "Visilux" 2 light over the entire surface for approximately two minutes or until the resin was completely tack-free. Immediately following the irradiation step, a two-part chemically curable impression material (Express Medium Viscosity Wash, Minnesota Mining and Manufacturing Company, St. Paul, Minnesota) was applied by syringe directly over the

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several teeth both adjacent to and including those previously irradiated with light. The material was allowed to set for about five minutes. The bulk
5 material was easily removed from the typodont by firmly holding the typodont in one hand and the impression in the other. Upon removal of the silicone impression, it was observed that the light-cured material was firmly and completely bonded to the chemically-cured material.
10 The stone model that was prepared from the impression showed improved detail where the light cured material was placed.

Various modifications and alterations of this
15 invention will become apparent to those skilled in the art without departing from the scope and spirit of this invention, and it should be understood that this invention is not to be unduly limited to the illustrated embodiments set forth herein.

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WHAT IS CLAIMED IS:

1. A hydrosilation process which comprises
 5 reacting a composition comprising a compound having
 aliphatic unsaturation and a compound containing at
 least one silicon-bonded hydrogen atom and not having
 more than three hydrogen atoms attached to any one
 silicon atom, in the presence of both a
 10 (η^5 -cyclopentadienyl)tri- (σ -aliphatic)platinum complex
 and a free-radical photoinitiator that is capable of
 absorbing actinic radiation such that the hydrosilation
 reaction is initiated upon exposure to actinic
 radiation.

15

2. The process of Claim 1, wherein said
 reaction is carried out by means of exposing said
 composition to actinic radiation having a wavelength of
 200 nm to 800 nm.

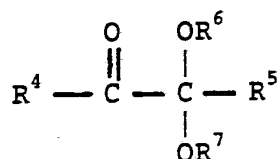
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3. The process of Claim 1, wherein said
 free-radical photoinitiator is a monoketal of an
 α -diketone or an α -ketoaldehyde.

25

4. The process of Claim 3, wherein said
 photoinitiator has the general formula:

30



35

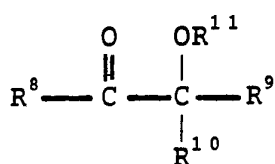
wherein R^4 represents an unsubstituted aryl group or an
 aryl group substituted with one or more groups that do
 not interfere with the hydrosilation reaction, R^5 , R^6 ,
 and R^7 each independently represents a member selected
 from the group consisting of unsubstituted aryl groups
 and aryl groups substituted with one or more groups that
 do not interfere with the hydrosilation reaction,

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aliphatic groups having from one to eighteen carbon atoms, and hydrogen.

5 5. The process of Claim 1, wherein said free-radical photoinitiator is an acyloin or an ether thereof.

6. The process of Claim 5, wherein said
10 photoinitiator has the general formula:



15

wherein R^8 represents an unsubstituted aryl group or an aryl group substituted with one or more groups that do not interfere with the hydrosilation reaction, and R^9 , R^{10} , and R^{11} each independently represents a member
20 selected from the group consisting of unsubstituted aryl groups or an aryl group substituted with one or more groups that do not interfere with the hydrosilation reaction, an aliphatic group having from one to eighteen carbon atoms, and hydrogen.
25

7. The process of Claim 1, wherein said composition further includes a sensitizer.

8. The process of Claim 7, wherein said
30 sensitizer is a polycyclic aromatic compound.

9. The process of Claim 8, wherein said polycyclic aromatic compound has from three to five rings, inclusive.
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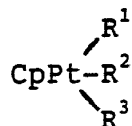
10. The process of Claim 9, wherein said polycyclic aromatic compound is selected from the group consisting of 9,10-dimethylantracene and
5 9,10-dichloroanthracene.

11. The process of Claim 7, wherein said sensitizer is an aromatic compound containing a ketone chromophore.
10

12. The process of Claim 11, wherein said aromatic compound is a thioxanthone.

13. The process of Claim 12, wherein said
15 thioxanthone is selected from the group consisting of 2-chlorothioxanthone and 2-isopropylthioxanthone.

14. The process of Claim 1, wherein the platinum complex has the formula:
20



25 wherein

Cp represents a cyclopentadienyl group that is eta-bonded to the platinum atom, the cyclopentadienyl group being unsubstituted or substituted with one or more groups that do
30 not interfere in a hydrosilation reaction, and each of R¹, R², and R³ represents an aliphatic group having from one to eighteen carbon atoms, said R¹, R², and R³ groups being sigma-bonded to the platinum atom.
35

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15. The process of Claim 14, wherein the platinum complex is selected from the group consisting of:

- 5 (η⁵-cyclopentadienyl)trimethylplatinum,
(η⁵-methylcyclopentadienyl)trimethylplatinum,
(η⁵-trimethylsilylcyclopentadienyl)trimethyl-
platinum, and
10 (η⁵-dimethylphenylsilylcyclopentadienyl)tri-
methylplatinum.

16. The process of Claim 1, wherein the composition comprises from about 0.1 to about 10.0 equivalent weights of the compound having silicon-bonded
15 hydrogen per equivalent weight of the compound having aliphatic unsaturation, and, per 1,000,000 parts by weight of the total composition, from about 5 to about 1000 parts by weight of the platinum catalyst, and from about 50 to about 50,000 parts by weight of the
20 free-radical photoinitiator.

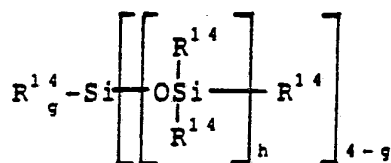
17. The process of Claim 7, wherein the composition comprises from about 0.1 to about 10.0 equivalent weights of the compound having silicon-bonded
25 hydrogen per equivalent weight of the compound having aliphatic unsaturation, and, per 1,000,000 parts by weight of the total composition, from about 5 to about 1000 parts by weight of the platinum catalyst, and from about 50 to about 50,000 parts by weight of the
30 free-radical photoinitiator, and from about 50 to about 50,000 parts by weight of said sensitizer.

35

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18. The process of Claim 1, wherein the compound containing aliphatic unsaturation is a polyorganosiloxane having the general formula:

5



10 where

each R^{14} can be the same or different and represents a non-halogenated or halogenated ethylenically-unsaturated group, a non-halogenated or halogenated alkyl group or cycloalkyl group, or a phenyl group, at least 70% of all R^{14} groups being methyl groups, but no more than 10% of all R^{14} groups being vinyl or other alkenyl, and at least two of the R^{14} groups being vinyl or other alkenyl,

15
20 h represents a number having a value from 1 to about 3000, and

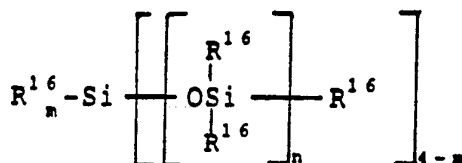
g represents 0, 1, 2, or 3.

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19. The process of Claim 1, wherein the compound containing silicon-bonded hydrogen is a polyorganohydrosiloxane having the general formula:



wherein

- each R^{16} can be the same or different and represents an alkyl group, a cycloalkyl group, a phenyl group, or hydrogen, at least two but no more than one-half of all the R^{16} groups in the siloxane being hydrogen,
- m represents 0, 1, 2 or 3, and
- n represents a number having an average value from one to about 3000.

20. The process of Claim 1, wherein the compound having aliphatic unsaturation is one having olefinic unsaturation.

21. A radiation-curable composition comprising:

(a) a silicon compound containing at least one hydrogen atom attached to silicon per molecule, there being not more than three hydrogen atoms attached to any one silicon atom,

(b) a compound containing aliphatic unsaturation,

(c) a (η^5 -cyclopentadienyl)tri(σ -aliphatic)platinum complex, and

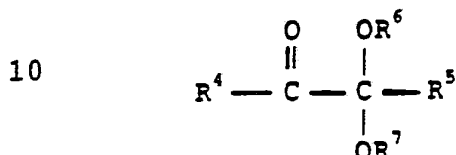
(d) a free-radical photoinitiator that is capable of absorbing actinic radiation.

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22. The composition of Claim 21, wherein said free-radical photoinitiator is a monoketal of an α -diketone or an α -ketoaldehyde.

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23. The composition of Claim 22, wherein said photoinitiator has the general formula:



15 wherein R^4 represents an unsubstituted aryl group or an aryl group substituted with one or more groups that do not interfere with the hydrosilation reaction, R^5 , R^6 , and R^7 each independently represents a member selected from the group consisting of unsubstituted aryl groups and aryl groups substituted with one or more groups that
20 do not interfere with the hydrosilation reaction, aliphatic groups having from one to eighteen carbon atoms, and hydrogen.

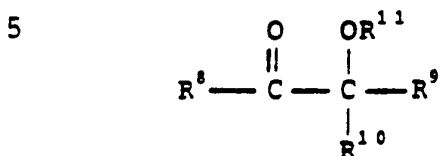
24. The composition of Claim 21, wherein said
25 free-radical photoinitiator is an acyloin or an ether thereof.

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25. The composition of Claim 24, wherein said photoinitiator has the general formula:



10 wherein R^8 represents an unsubstituted aryl group or an aryl group substituted with one or more groups that do not interfere with the hydrosilation reaction, and R^9 , R^{10} , and R^{11} each independently represents a member
15 groups and aryl groups substituted with one or more groups that do not interfere with the hydrosilation reaction, an aliphatic group having from one to eighteen carbon atoms, and hydrogen.

20 26. The composition of Claim 21, further including a sensitizer.

25 27. The composition of Claim 26, wherein said sensitizer is a polycyclic aromatic compound.

28. The composition of Claim 27, wherein said polycyclic aromatic compound has from three to five rings, inclusive.

30 29. The composition of Claim 28, wherein said polycyclic aromatic compound is selected from the group consisting of 9,10-dimethylantracene and 9,10-dichloroanthracene.

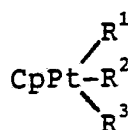
35 30. The composition of Claim 26, wherein said sensitizer is an aromatic compound containing a ketone chromophore.

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31. The composition of Claim 30, wherein said aromatic compound is a thioxanthone.

5 32. The composition of Claim 31, wherein said thioxanthone is selected from the group consisting of 2-chlorothioxanthone and 2-isopropylthioxanthone.

10 33. The composition of Claim 21, wherein the platinum complex has the formula:



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wherein

20 Cp represents a cyclopentadienyl group that is eta-bonded to the platinum atom, the cyclopentadienyl group being unsubstituted or substituted with one or more groups that do not interfere in a hydrosilation reaction, and each of R¹, R², and R³ represents an aliphatic group having from one to eighteen carbon atoms, said R¹, R², and R³ groups being sigma-bonded to the platinum atom.

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34. The composition of Claim 33, wherein the platinum complex is selected from the group consisting of:

30 (η⁵-cyclopentadienyl)trimethylplatinum,
 (η⁵-methylcyclopentadienyl)trimethylplatinum,
 (η⁵-trimethylsilylcyclopentadienyl)trimethyl-
 platinum, and
 (η⁵-dimethylphenylsilylcyclopentadienyl)tri-
35 methylplatinum.

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35. The composition of Claim 21, said composition comprising from about 0.1 to about 10.0 equivalent weights of the compound having silicon-bonded hydrogen per equivalent weight of the compound having aliphatic unsaturation, and per 1,000,000 parts by weight of the total composition, from about 5 to about 1000 parts by weight of the platinum complex and from about 50 to about 50,000 parts by weight of the free-radical photoinitiator.

36. The composition of Claim 26, said composition comprising from about 0.1 to about 10.0 equivalent weights of the compound having silicon-bonded hydrogen per equivalent weight of the compound having aliphatic unsaturation, and per 1,000,000 parts by weight of the total composition, from about 5 to about 1,000 parts by weight of the platinum complex and from about 50 to about 50,000 parts by weight of the free-radical photoinitiator, and from about 50 to about 50,000 parts by weight of said sensitizer.

37. A dental impression prepared by exposing the composition of Claim 21 to actinic radiation.

38. A substrate bearing on at least one major surface a layer prepared by applying the composition of Claim 21 to said surface and then exposing said composition to actinic radiation.

39. A pressure-sensitive adhesive tape comprising a backing bearing on one major surface thereof a layer of normally tacky and pressure-sensitive adhesive, and bearing on the other major surface thereof a release surface prepared by applying on said other major surface the composition of Claim 21 and then exposing said composition to actinic radiation.

SUBSTITUTE SHEET

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40. An adhesive tape comprising a backing bearing on at least one major surface thereof a silicone adhesive prepared by applying on said at least one major surface the composition of Claim 21 and then exposing said composition to actinic radiation.

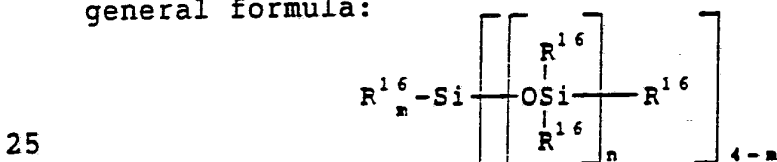
41. The tape of Claim 40, wherein said silicone adhesive is a pressure-sensitive adhesive.

42. A gasket prepared by exposing the composition of Claim 21 to actinic radiation.

43. An adhesive prepared by exposing the composition of Claim 21 to actinic radiation.

44. A conformal coating prepared by exposing the composition of Claim 21 to actinic radiation.

45. Radiation-curable composition comprising (a) a polyorganohydrosiloxane having the general formula:



wherein

each R^{16} can be the same or different and represents

an alkyl group, a cycloalkyl group, a phenyl group, or hydrogen, at least two but no more than one-half of all the R^{16} groups in the siloxane being hydrogen,

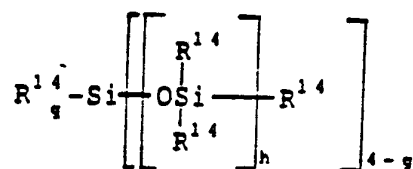
m represents 0, 1, 2 or 3, and

n represents a number having an average value from one to

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about 3000,

(b) a polyorganosiloxane having the general formula:



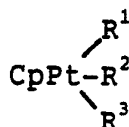
wherein

each R^{14} can be the same or different and represents a non-halogenated or halogenated ethylenically unsaturated group, a non-halogenated or halogenated alkyl group or cycloalkyl group, or the phenyl group, at least 70% of all R^{14} group being methyl groups, but no more than 10% of all R^{14} groups being vinyl or other alkenyl, and at least two of the R^{14} groups being vinyl or other alkenyl,

h represents a number having a value from 1 to about 3000, and

g represents 0, 1, 2, or 3,

(c) a platinum complex represented by the formula:



wherein

Cp represents a cyclopentadienyl group that is eta-bonded to the platinum atom, the cyclopentadienyl group being unsubstituted or substituted with one or more groups that do not interfere in a hydrosilation reaction, and each of R^1 , R^2 , and R^3 represents an aliphatic

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group having from one to eighteen carbon atoms, said R^1 , R^2 , and R^3 groups being sigma-bonded to the platinum atom,

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(d) a free-radical photoinitiator that is capable of absorbing actinic radiation.

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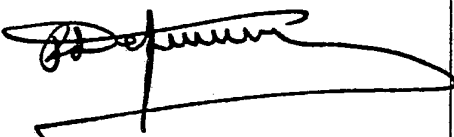
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INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 91/08436

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) ⁶		
According to International Patent Classification (IPC) or to both National Classification and IPC		
Int. Cl. 5	C08L83/07; C07F/08	C08G77/38; C08K5/56; C08K5/00
II. FIELDS SEARCHED		
Minimum Documentation Searched ⁷		
Classification System	Classification Symbols	
Int. Cl. 5	C08L ; C08G ; C08K ; C07F	
Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched ⁸		
III. DOCUMENTS CONSIDERED TO BE RELEVANT⁹		
Category ^o	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³
Y, D	EP, A, 0 358 452 (MINNESOTA MINING AND MANUFACTURING COMPANY) 14 March 1990 see claims 1-29 see page 4, line 19 - page 5, line 10 ---	1, 2, 7-21, 26-45
Y, D	EP, A, 0 146 307 (MINNESOTA MINING AND MANUFACTURING COMPANY) 26 June 1985 see claims 1, 2, 4, 5-16 see page 8, line 12 - page 9, line 36 see page 16, line 12, paragraph 19 ---	1, 2, 7-21, 26-45
Y	DE, A, 2 736 499 (WACKER-CHEMIE GMBH.) 22 February 1979 see claim 1 see page 10, paragraph 1-3 see page 18, paragraph 1-3 ---	1, 2, 7-21, 26-45
-/--		
^o Special categories of cited documents : ¹⁰ "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier document but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art. "&" document member of the same patent family		
IV. CERTIFICATION		
Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report	
19 FEBRUARY 1992	27. 02. 92	
International Searching Authority	Signature of Authorized Officer	
EUROPEAN PATENT OFFICE	DEPIJPER R.D.C.	

III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)		
Category ^a	Citation of Document, with indication, where appropriate, of the relevant passages	Relevant to Claim No.
A	EP,A,0 398 701 (MINNESOTA MINING AND MANUFACTURING COMPANY) 22 November 1990 see claims 1-18 ---	1
A	EP,A,0 153 700 (TORAY SILICONE COMPANY LTD.) 4 September 1985 see claims 1,2,6,8 see page 5, line 25 - page 6, line 10 --- 	1

**ANNEX TO THE INTERNATIONAL SEARCH REPORT
ON INTERNATIONAL PATENT APPLICATION NO.**

US 9108436
SA 54188

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report. The members are as contained in the European Patent Office EDP file on
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information. 19/02/92

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