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(54) Title
TIN CATALYST OBTAINED FROM A TIN OXIDE AND A BETA-DICARBONYL COMPOUND USEFUL FOR SILICONE ELASTOMER COMPOSITIONS

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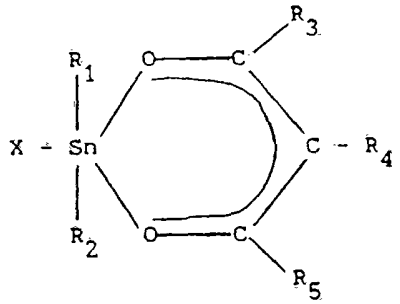
(57) Claim

1. A monochelate of pentacoordinated tin of valency IV, of formula:



(1)

in which:

- R_1 and R_2, which are the same or different denote unsubstituted or substituted monovalent C_1-C_{18} organic hydrocarbon radicals,
- R_3 and R_5, which are the same or different, are chosen from radicals R_1 and R_2, hydrogen, C_1-C_5 alkoxy radicals or

.../2

silyl radicals $Si(R_1)_3$,

- R_4 is hydrogen, an optionally halogenated C_1-C_8 hydrocarbon radical, or R_4 and R_5, together with the carbon atoms to which they are attached, form a divalent C_5-C_{12} cyclic hydrocarbon radical unsubstituted or substituted by chlorine, nitro or cyano, and

- X is a monocarboxylate radical of formula R_6COO in which R_6 has the same meaning as R_1 above.

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COMPLETE SPECIFICATION FOR THE INVENTION ENTITLED:

"TIN CATALYST OBTAINED FROM A TIN OXIDE AND A β-DICARBONYL COMPOUND USEFUL FOR SILICONE ELASTOMER COMPOSITIONS"

The following statement is a full description of this invention, including the best method of performing it known to us :-

This invention relates to novel monochelates of tin, and silicone compositions containing them. Many tin compounds have already been proposed as catalysts for crosslinking polyorganosiloxane compositions and in particular RTV compositions (room temperature vulcanizable compositions), in a single pack or in two packs, otherwise known as single - or two-component compositions.

The most widely used compounds are tin carboxylates such as tributyltin monooleate, tin 2-ethylhexanoate or dialkyltin dicarboxylates such as dibutyltin diacetate (see the work by Noll "Chemistry and Technology of Silicones", page 337, Academic Press, 1968 - 2nd edition).

According to US Patent 3, 186,963, the tin catalyst proposed is the product of the reaction of a dialkyldialkoxysilane with a dialkyltin carboxylate.

According to Belgian Patent BE-A-842,305, the catalyst proposed is the product of the reaction of an alkly silicate or of an alkyltrialkoxysilane with dibutyltin diacetate.

According to US Patent 3,708,467, a catalyst system is described, consisting of a mixture of certain tin salts with a specific titanium chelate, in a single component

composition.

Lastly, the use of diorganotin bis(β-diketone) is described in US Patents 4,517,337 and 4,554,310 for crosslinking neutral single-component compositions and in EP-A-147,323 for crosslinking single- and two component compositions.

Although the invention of EP-A-147,323 has made it possible to achieve considerable progress in the search for a tin catalyst capable of being employed both for single- and two-component compositions, it has become apparent that diorganotin bis(β-diketonates) exhibit a core setting time which is a little slow, particularly in the case of the two-component compositions.

The problem which arises generally in the case of the single-component compositions is essentially that of the storage stability and of the retention of the physicochemical properties (extrudability, pourability, setting time) of the composition and retention of these properties by the cross-linked product (mechanical properties, hardness, elongation, tear strength, adhesiveness, and the like).

It is therefore desirable to find a catalyst which crosslinks the composition very rapidly on exposure to atmospheric moisture on its surface, but which at the same time provides a thorough crosslinking throughout the composition which is as complete as possible, and which is

active in a low dosage in order to reduce to the minimum the degradation of the cross-linked product which is inherent in the presence of tin.

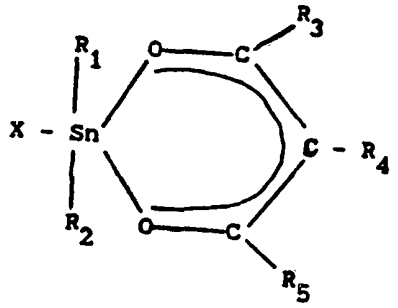
So far as the cross-linked product is concerned, the same problems exist in the case of the two-component compositions as with single-component compositions; but in addition, the pot life, that is to say the time during which the composition may be employed after mixing without hardening, must be sufficiently long to permit its use, but sufficiently short to produce a moulded object capable of being handled not later than 24 hours after its production.

The catalyst must therefore make it possible to obtain a good compromise between the pot life of the catalysed mixture and the time after which the moulded object can be handled. In addition, the catalyst must confer on the catalysed mixture a spreading time which does not vary as a function of the storage period.

The present invention provides a catalyst system capable of being employed in the crosslinking both of single- and two-component elastomer compositions, and thus simplifies the industrial production of such compositions.

The new catalyst system meets to a high degree the storage, use and crosslinking requirements of both types of compositions without, however, introducing detrimental secondary effects in either case.

The present invention provides organopolysiloxane compositions comprising a silicone base capable of being cured to an elastomer by a polycondensation reaction starting at ambient temperature and a catalytically effective quantity of a monochelate of pentacoordinated tin of valency IV, of formula:



(1)

in which: the symbols R_1 and R_2, which are identical or different, each denote unsubstituted or substituted monovalent C_1-C_{18} organic hydrocarbon radicals, including:

- C_1-C_{18} alkyl radicals, halogenated or otherwise, such as methyl, ethyl, propyl, isopropyl, butyl, isobutyl, secondary butyl, tert-butyl, pentyl, hexyl, heptyl,2-ethylhexyl, octyl, decyl, dodecyl, octadecyl, chloromethyl and 2,5-dichloroethyl radicals,

- C_2-C_{18} alkenyl radicals, halogenated or otherwise, such as vinyl, allyl, methallyl, 2-butenyl, 2-pentenyl, 3-octenyl, 5-fluoro-2-pentenyl and pentadecenyl radicals,

- C_4-C_{10} cycloalkyl radicals, halogenated or otherwise, such as cyclopentyl, cyclohexyl, methylcyclohexyl, cyclooctyl, 3,4-dichlorocyclohexyl and 2,6-dibromocycloheptyl radicals,

- C_6-C_{15} mononuclear aryl radicals, halogenated or otherwise, such as phenyl, tolyl, xylyl, cumenyl, chlorophenyl, dichlorophenyl, trichlorophenyl, difluorophenyl and trifluoromethlphenyl radicals,

- C_7-C_{15} mononuclear arylalkyl radicals, halogenated or otherwise, such as phenyl, phenylethyl, phenylpropyl and trifluoromethylphenylethyl radicals.

R_3 and R_5, which are identical or different, are each unsubstitued or substituted monovalent C_1-C_{18} organic hydrocarbon radicals, such as those described above, hydrogen cyanoalkyl radicals containing a C_2-C_4 alkyl moiety, C_1-C_5 alkoxy radicals or $-Si(R_1)_3$ silyl radicals.

Cyanoethyl, cyanopropyl and cyanobutyl radicals may be mentioned by way of illustration of cyamoalkyl radicals, and ethoxy and propoxy radicals may be mentioned as alkoxy radicals.

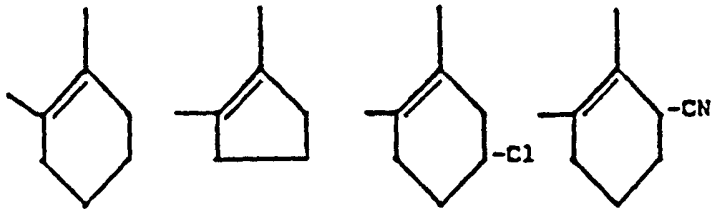
R_4 denotes hydrogen, or an optionally halogenated C_1-C_8 hydrocarbon radical.

More especially, this radical includes alkyl radicals, halogenated or otherwise, such as methyl, ethyl, propyl, butyl, hexyl, and octyl radicals and mononuclear aryl radicals, halogenated or otherwise, such as phenyl,

tolyl, chlorophenyl and dichlorophenyl radicals.

In addition, on coupling with R_5, R_4 forms with R_5 and the carbon atoms to which they are attached a divalent cyclic C_5- C_{12} hydrocarbon radical, substituted or otherwise by chloro, nitro or cyano radicals.

To illustrate these rings there may be mentioned those of formulae:



The symbol X a monocarboxylate radical of formula R_6COO in which the symbol R_6 has the same meaning as the symbol R_1 above and preferably denotes a linear or branched C_1-C_{18} alkyl radical.

So far as the Applicant Company is aware, the monochelates of formula (1) are new products.

These monochelates may be identified by analytical techniques of NMR spectroscopy (^{119}Sn, ^{13}C and ^{1}H nuclear magnetic resonance) and by mass spectroscopy and by measurement of the Mossbauer effect.

It has been found, however, that in the present state of knowledge of analytical techniques, the ^{119}Sn NMR analytical method such as described, in particular, in the article by Peter J. Smith, "Chemical Shifts of ^{119}Sn

Nuclei in Organotin Compounds", page 291 et seq, published in the Annual Reports on NMR Spectroscopy, volume 8, 1978, Academic Press, is a method which is by itself sufficiently accurate to characterize the various tin compounds present within a mixture, especially within a reaction mixture, and to make it possible to find the chemical formulae of most of these compounds.

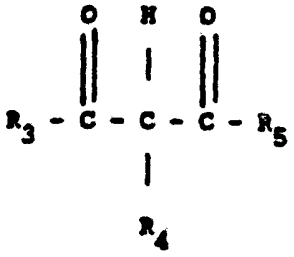
The fundamental parameter evaluated by ^{119}Sn NMR is the value of the chemical shift, expressed in parts per million (ppm) relative to a reference (generally tetramethyltin).

The value of the chemical shift is particularly sensitive to the electronegativity of the groups carried by the tin and to the change in the coordination number of the tin atom. Specific studies of characterization of organostannic derivatives using ^{119}Sn NMR are described in particular by A.G. Davies and P.J. Smith, Comprehensive Organo-metallic Chemistry 11 Tin, pages 523 to 529 and by J. Otera, J. of Organomet. Chem. 221, pages 57-61 (1981).

The monochelates are obtained by reaction of a tin oxide of formula:

$$R_1R_2SnO \qquad (2)$$

with a ß-dicarbonyl of formula:



(3)

symbolized below by the simplified formula CH, and an organic acid of formula:

XH (4)

in which formulae R_1, R_2, R_3, R_4, R_5 and X have the definition given above, with removal of the water formed.

This reaction may, for example, take place in bulk or in an organic solvent (for example cyclohexane), with removal of water at the reflux temperature of the solvent employed.

The reaction may be performed by reaching the starting materials (3) and (4) in a molar ratio (3)/(4) of between 0.01 to 100, preferably between 0.1 and 10, and still more preferably between 0.4 and 2.5.

The compound (2) is added so that the molar ratio (2)/[(3) + (4)] is between 1/0.8 and 1/3.

The process of the invention may, for example, be carried out simply by mixing the starting materials (2), (3) and (4) in a closed reactor in the absence of atmospheric moisture, with the removal of water. The reaction can take place starting at ambient temperature. It is desirable, however, to raise the temperature of the reaction mixture to a value which is generally between 70 and 120°C to accelerate the reaction kinetics and/or to remove the water formed and/or to solubilize a starting material which is in the solid state at ambient temperature.

The water formed may be removed by any known means, particularly by distilling the reaction mixture at

a reduced pressure of between 0.01 and 10 kPa for a period which depends on the quality of the vacuum employed.

The water formed may also be removed by azeotropic distillation at the reflux temperature of the solvent employed.

According to an alternative form of the invention, the reaction of the products of formula (2), (3) and (4) may be carried out not in a single stage but in two stages.

During the first stage the tin oxide of formula (2) is reacted with the acid of formula (4) to obtain, after removal of the water formed, a distannoxane of formula (5):

$$XR_1R_2SnOSnR_1R_2X \qquad (5)$$

in which X, R_1 and R_2 have the meaning given above.

During the second stage the distannoxane of formula (5) is reacted with the β-dicarbonyl compound of formula (3) and the desired reaction mixture is obtained after removal of the water formed, comprising the tin monochelate of formula (1).

The conditions in which these two stages are carried out are analogous to those which can be employed for the single-stage process.

The molar ratio (2)/(4) is preferably equal to or very close to 1 and the molar ratio of (5)/(3) is generally between 1 and 1.5.

Specific examples of tin oxides of formula (2)

which may be employed include dimethyltin oxide, diethyltin oxide, dipropyltin oxide, dibutyltin oxide, di(2-ethylhexyl)tin oxide, dilauryltin oxide, dipropenyltin oxide, diphenyltin oxide, ditolyltin oxide, methylethyltin oxide and phenylbutyltin oxide.

Examples of ß-dicarbonyl compounds, ß-diketones and ß-ketoesters of formula (3) which are within the scope of the invention include: 2,4-heptanedione, 2,4-decanedione, 2-methyl-2-decene-6,8-dione, 2-methyl-2-nonene-6,8-dione, 1-stearoyl-2-octanone, triacetylmethane, ethyl 7,9-dioxodecanoate, benzoylacetone, 1-benzoyl-2-octanone, 1,4-diphenyl-1,3-butanedione, stearoylacetophenone, palmitoylacetophenone, 1-benzoyl-4-methyl-2-pentanone, benzoylocosanoylmethane, 1,4-bis(2,4-dioxobutyl)benzene, paramethoxybenzoylstearoylmethane, 2-allyl-1-phenyl-1,3-butanedione, 2-methyl-2-acetylacetaldehyde, benzoylacetaldehyde, acetoacetyl-3-cyclohexene, bis(2,6-dioxocyclohexyl)methane, 2-acetyl-1-oxo-1,2,3,4-tetrahydronaphthalene, 2-palmitoyl-1-oxo-1,2,3,4-tetrahydronaphthalene, 1-oxo-2-stearoyl-1,2,3,4-tetrahydronaphthalene, 2-acetyl-1-cyclohexanone, 2-benzoyl-1-cyclohexanone, 2-acetyl-1,3-cyclohexanedione, dibenzoylmethane, tribenzoylmethane, bis(para-methoxybenzoyl)methane, 1-(N-phenylcarbamoyl)-1-benzoylacetone, 1-(N-phenylcarbamoyl)-1-acetylacetone, ethyl acetylacetate, acetylacetone and 1,1,1-trifluoro-3-benzoylacetone.

These various β-diketones of formula (3) are usually prepared by various known procedures, such as those described in "Organic Reactions" by R. Adams et al (1954 edition, volume VIII, pages 59 et seq). Certain more specific syntheses are described in Rec. Trav. Chim. Pays-Bas (1897) volume 16, pages 116 et seq, by M.J. Kramers, in J. Chem. Soc. (1925) volume 127, pages 2891 et seq, by G.T. Morgan et al, or in J. Chem. Soc. (1941), pages 1582 et seq, by R. Robinson and E. Seijo.

Specific examples of acids of formula (4) which are within the scope of the present invention include:

- saturated acids such as formic, acetic, propionic, butyric, isobutyric, valeric, isovaleric, pivalic, lauric, 2-ethylhexanoic, myristic, palmitic and stearic acids or versatic R acids, which are mixtures of saturated tertiary monocarboxylic acids containing, overall, the same number of carbon atoms, which is generally between 8 and 12,
- unsaturated acids such as acrylic, propiolic ($CH\equiv C-COOH$), methacrylic, crotonic, isocrotonic, oleic or maleic acids,
- carbocyclic acids such as benzoic, phthalic, isophthalic or terephthalic acids, and
- organic diacids.

The monochelate of formula (1) may be obtained as practically pure material or in equilibrium with the starting materials and/or the reaction by-products.

It has been demonstrated that the equilibrium reaction mixture of the invention obtained is capable of being employed in a catalytically effective quantity for curing silicone bases.

Using ^{119}Sn NMR, it is found that, in general, in addition to the pentacoordinated monochelate R_1R_2SnCX, the equilibrium reaction mixture contains the di-stannoxane $XR_1R_2SnOSnR_1R_2S$, the diorganotin di-carboxylate or dihalide $R_1R_2SnC_2$, as tin compound. When a molar ratio of starting materials (3)/(4) of between 0.5 and 1.5, and a molar ratio (2)/[(3) + (4)] of between 1/1 and 1/2.5 is used, the concentrations of the constituents of the reaction mixture in molar %, calculated in gram-atoms of tin metal are, in principle:

R_1R_2SnCX	30 to 95
$R_1R_2SnX_2$	30 to 5
$R_1R_2SnC_2$	30 to 0
$XR_1R_2SnOSnR_1R_2X$	10 to 0

Unless mentioned otherwise, the percentages and parts in what follows are by weight.

The monochelate of formula (1) or the equilibrium reaction mixture, referrred to below as the tin catalyst according to the invention, is stable in storage in a closed container, at ambient temperature.

It is employed to permit or facilitate the curing

of the organopolysiloxane base to a silicone elastomer, starting at ambient temperature.

These bases, which cure (crosslink) by polycondensation reactions are well known. After catalysed curing in most cases using a metallic derivative. of a carboxylic acid, they are employed for the manufacture of seals, of water-repellent coatings, of moulds, of coating materials, for the adhesive bonding and the assembly of the widest variety of materials, for coating organic and inorganic fibres, and the like.

These bases are described in detail and they are available commercially.

These silicone bases may be single-component, that is to say packaged in a single pack, in which case they are stable in storage in the absence of moisture and capable of being used in the presence of moisture, in particular of moisture contributed by the surrounding air or by the water generated within the base when it is used.

These single-component bases are generally of three types, as described in further detail below, and are catalysed by the incorporation of a catalytically effective quantity of monochelate of formula (1) or of the equilibrium mixture containing the product of formula (1). This catalytically effective quantity is of the order of 0.0001 to 5, preferably from 0.01 to 3 parts per 100 parts of the single-component base.

Apart from the single-component bases, it is also

possible to employ two-component bases, which are packaged in two packs, and which cure as soon as the tin catalyst is incorporated. They are packaged in two separate fractions, with, for example, one fraction containing only the tin catalyst or the mixture of the catalyst with the cross-linking agent.

The catalytically effective quantity of tin catalyst is of the order of 0.01 to 10 parts, preferably from 0.1 to 5 parts per 100 parts of the two-component base.

As already indicated above, single-component and two-component silicone bases which cure (crosslink) via polycondensation reactions are described in detail in the literature and are available commercially.

These bases are generally prepared from the following constituents:

A. - 100 parts of an α,ω-dihydroxypolydiorganosiloxane polymer, with a viscosity of 500 to 1,000,000 mPa s at 25°C, consisting of a succession of $(R_2)SiO$ units where the symbols R, which are identical or different, denote hydrocarbon radicals containing from 1 to 10 carbon atoms, optionally substituted by halogen atoms or cyano groups,

B. - 0.5 to 20 parts of a crosslinking agent chosen from organosilicon compounds bearing more than two hydrolysable groups linked to the silicon atoms, per molecule,

C. - 0 to 250 parts of inorganic fillers, and

D. - 0 to 20 parts of an adhesion promoter.

The radical R is generally methyl, ethyl, propyl, phenyl, vinyl or 3,3,3-trifluoropropyl radicals, at least 80% of the groups R being methyl.

A first type of single-component formula results from mixing the polymer A with a crosslinking agent B, which is a silane of formula:

$$R_aSi(Z)_{4-a} \qquad (6)$$

in which R has the definition given above for the polymer A, and Z is a hydrolysable group generally chosen from N-substituted amino, N-substituted amido, N,N-disubstituted aminoxy, ketiminoxy, aldiminoxy, alkoxy, alkoxyalkylenoxy, enoxy and acyloxy groups, and a denotes 0 or 1.

Single-component bases of this type are described in detail, particularly in European Patent Applications EP-A-141,685 and EP-A-147,323, to which reference may be made.

The most widely used compositions are those in which Z is an acyloxy and ketiminoxy group, which are described in greater detail particularly in European Patent Application EP-A-102,268, to which reference may be made.

Two-component flowing compositions, in which Z is an acyloxy group, and whose crosslinking is accelerated by the addition of an alkaline-earth metal hydroxide or phosphate are described in European Patent Applications EP-A-118,325 and EP-A-117,772, to which reference may

be made.

According to a second type of single-component base, the starting point is not a mixture of A and B but the product A_1 of reaction of A with B. In general, the hydrolysable group is an alkoxy group and the composition additionally contains from 0 to 15 parts of cross-linking agent B per 100 parts of functionalized polymer A_1.

The reaction of A with B can take place in the presence of various catalysts such as an organic amine (US Patent US-A-3,542,901), an organic titanium derivative (US Patent US-A-4,111,890), a carbamate (European Patent Application EP-A-210,402) and an N,N-disubstituted hydroxylamine (European Patent Application EP-A-70,786).

To these single-component bases there may be added adhesion promoters D, chosen from organosilicon compounds simultaneously bearing, on the one hand, organic groups substituted by radicals chosen from the group of amino, ureido, isocyanate, epoxy, alkenyl, isocyanurate, hydantoyl, guanidino and mercaptoester radicals and, on the other hand, hydrolysable groups, generally alkoxy groups linked to the silicon atoms. Examples of such adhesion promoters are described in US Patents US-A-3,517,001, US-A-4,115,356, US-A-4,180,642, US-A-4,273,698 and US-A-4,356,116, and in European Patent Applications EP-A-31,996 and EP-A-74,001.

A third type of single-component bases are those

prepared by mixing 100 parts of polymer A, from 0.5 to 20 parts of crosslinking agent B which is a polyalkoxysilane (formula 4), Z = alkoxy or alkoxyalkyleneoxy, from 0 to 250 parts of inorganic fillers and from 0.5 to 15 parts of a compound D_1 chosen from:

- D_{1-a} a primary organic amine having a pKb of less than 5 in aqueous medium, an aminoorganosilane and an aminoorganopolysiloxane bearing at least one C_1-C_{15} organic group linked by a Si-C bond to the silicon atom per molecule, and substituted by at least one amino radical, and at least one C_1-C_5 alkoxy or C_3-C_6 alkoxy alkyleneoxy radical, and

- D_{1-b} an organic titanium and zirconium derivative bearing an organoxy and/or β-diketonato group.

Single-component bases comprising D_{1-a} are described in European Patent Application EP-A-21,859, and those comprising D_{1-b} are described in French Patents FR-A-2,121,289 and FR-A-2,121,631, to which reference may be made.

The two-component bases are formed by mixing:

a) - 100 parts of polymer (A),

b) - 1 to 20 parts of a crosslinking agent chosen from:

a silane of formula (6) above,

the products of partial hydrolysis of the silane of formula (6),

c) - 0 to 150 parts of inorganic fillers, and

d) - 0 to 20 parts of an adhesion promoter.

These compositions are well known; in particular, they are described in Europen Patent Applications EP-A-10,478, EP-A-50,358 and EP-A-184,966 and in US Patents US-A-3,801,572 and US-A-3,888,815, to which reference may be made.

The adhesion promoter employed may be the silanes D employed in the case of the single-component bases and silanes bearing a morpholino group (EP-A-184, 966) or an organic radical comprising a tertiary nitrogen atom (US-A-3,801,572 and US-A-3,888,815).

The products of partial hydrolysis of the alkoxysilanes of formula (4), which are usually referred to as alkyl polysilicates, are well-known products which exhibit the property of dissolving in the usual hydrocarbon solvents such as toluene, xylene, cyclohexane and methylcyclohexane; the most widely used product is ethyl polysilicate 40® (available from Union Carbide) with a silica content of 40%, a value obtained after total hydrolysis of the ethoxy radicals.

The inorganic fillers c) employed in the case of the single- and two-component bases are very finely divided products whose mean particle diameter is below 0.1 micrometre. These fillers include combustion silicas and precipitated silicas; their BET specific surface area is generally greater than 40 m^2/g.

If desired, these fillers may be in the form of more coarsely divided products, with a mean particle

diameter greater than 0.1 micrometre. Examples of such fillers which may be mentioned are ground quartz, diatomaceous silicas, calcium carbonate, calcined clay, rutile-type titanium oxide, iron, zinc, chromium, zirconium and magnesium oxides, the various forms of alumina (hydrated or otherwise), boron nitride, lithopone, barium metaborate, barium sulphate and ballotini; their specific surface area is generally below 30 m^2/g.

These fillers may have been surface-modified by treatment with the various organosilicon compounds usually employed for this purpose. Thus, these organosilicon compounds may be organochlorosilanes, diorganocyclopolysiloxanes, hexaorganodisiloxanes, hexaorganodisilazanes or diorganocyclopolysilazanes (French Patents FR-A-1,136,884, FR-A-1,136,885, FR-A-1,236,505, British Patent GB-A-1,024,234). In most cases, the treated fillers contain from 3 to 30% of their weight of organosilicon compounds.

The fillers may consist of a mixture of a number of types of fillers of different particle size distribution; thus, for example, they may consist of 30 to 70% of finely divided silicas with a BET specific surface area greater than 40 m^2/g and of 70 to 30% of more coarsely divided silicas with a specific surface area below 30 m^2/g.

The tin catalyst according to the invention is more particularly effective in the case of the single- and two-component silicone bases where the crosslinking

agent (B) of formula (6) contains radicals Z which are identical or different, chosen from alkoxy and alkoxy-alkylenoxy radicals of formulae R_7O and R_7OTO in which R_7 is a C_1-C_4 alkyl radical and T denotes a C_2-C_4 alkylene group.

In addition, in the case where the silicone base has two components it is possible to use the product of partial hydrolysis of the crosslinking agent (B).

In addition to the fundamental constituents of the single-component and two-component bases, that is to say (1) the diorganopolysiloxane polymers (A) and/or (A_1) blocked by a hydroxyl radical and/or alkoxyl radicals at the end of a chain, (2) the organosilicon crosslinking agents (B) bearing hydrolysable groups, (3) the inorganic fillers and (4) the adhesion promoters (D), other ingredients may be introduced.

These ingredients include organosilicon compounds, chiefly polymers, which are capable of affecting the physical characteristics of the compositions according to the invention (formed by mixing the bases with the tin catalyst) and/or the mechanical properties of the silicone elastomers obtained using these compositions.

These compounds are well known; for example they include:

-α,ω-bis(triorganosiloxy)diorganopolysiloxane polymers with a viscosity of at least 10 mPa s at 25°C in which the organic radicals linked to the silicon atoms are

chosen from methyl, vinyl or phenyl radicals, preferably at least 80% of the radicals are methyl radicals and not more than 3% arevinyl radicals; α,ω-bis(trimethylsiloxy)dimethylpolysiloxane oils with a viscosity of 10 mPa s at 25°C to 1,500 mPa s at 25°C are preferably employed;

- liquid, branched methylpolysiloxane polymers containing from 0.1 to 8% of hydroxyl groups linked to the silicon atoms, consisting of $(CH_3)_3SiO_{0.5}$, $(CH_3)_2SiO$ and $CH_3SiO_{1.5}$ units distributed so as to give a $(CH_3)_3SiO_{0.5}/(CH_3)_2SiO$ ratio of 0.01 to 0.15 and a $CH_3SiO_{1.5}/(CH_3)_2SiO$ ratio of 0.1 to 1.5;

-α,ω-di(hydroxy)dimethylpolysiloxane oils with a viscosity of 10 to 300 mPa s at 25°C and α,ω-di(hydroxy)-methylphenylpolysiloxane oils with a viscosity of 200 to 5,000 mPa s at 25°C; and

- diphenylsilanediol or 1,1,3,3-tetramethyldisiloxanediol.

The above α,ω-bis(triorganosiloxy)diorganopolysiloxane polymers may be completely or partly replaced by organic compounds which are inert towards the various constitutents of the bases and which are miscible at least with the diorganopolysiloxane polymers (A) or (A_1). Concrete examples of these organic compounds which may be mentioned are mineral oils, petroleum cuts and polyalkylbenzenes obtained by the alkylation of benzene with long-chain olefins, particularly olefins containing 12 carbon

atoms obtained by propylene polymerization. Organic compounds of this type appear, for example, in French Patents FR-A-2,392,476 and FR-A-2,446,849.

Each of the above organosilicon compounds may be employed in a proportion of 1 to 150 parts, preferably 3 to 75 parts, per 100 parts of diorganopolysiloxanes (A) or (A_1).

Non-organosilicon ingredients may also be introduced, for example heat stabilizers. These compounds improve the heat resistance of the silicone elastomers. They may be chosen from carboxylic acid salts, rare-earth oxides and hydroxides and more especially ceric oxides and hydroxides, as well from combustion titanium dioxide and various iron oxides. From 0.1 to 15 parts, preferably from 0.15 to 12 parts of heat stabilizers are advantageously employed per 100 parts of the diorganopolysiloxanes (A) or (A_1).

In the case of the single-component compositions, to manufacture the compositions according to the invention it is necessary to employ an equipment which enables the various fundamental constituents, to which the above-mentioned adjuvants and additives are added if desired, to be intimately mixed in the absence of moisture, with and without an input of heat.

All these ingredients may be charged into the equipment in any order of addition. Thus, the diorganopolysiloxane polymers (A) or (A_1) and the fillers (C) can

first be mixed, and the crosslinkers (B), the compounds (D) and the tin catalyst can then be added to the paste obtained.

It is also possible to mix the polymers (A) or (A_1), the crosslinkers (B) and the compounds (D) and subsequently to add the fillers (C) and the tin catalyst. The mixtures may be heated during these operations to a temperature in the range 50-180°C at atmospheric pressure or at a reduced pressure in order to promote the elimination of volatile substances such as water and polymers of low molecular weight.

The compositions prepared in this manner may be employed as such or in the form of a dispersion in organic diluents. These diluents are preferably conventional commercial products chosen from:

- aliphatic, cycloaliphatic or aromatic hydrocarbons, halogenated or otherwise, such as n-heptane, n-octane, cyclohexane, methylcyclohexane, toluene, xylene, mesitylene, cumene, tetralin, decalin perchloroethylene trichloroethane tetrachloroethane, chlorobenzene and orthodichlorobenzene;
- aliphatic and cycloaliphatic ketones such as methyl ethyl ketone, methyl isobutyl ketone, cyclohexanone and isophorone;
- esters such as ethyl acetate, butyl acetate and ethylglycol acetate.

The quantities of diluents introduced must be

sufficient to produce stable dispersions which spread easily on the substrates. These quantities depend essentially on the nature and on the viscosity of the initial organopolysiloxane compositions. They may consequently vary within wide proportions; nevertheless, manufacture of dispersions containing from 15 to 85% by weight of diluents is recommended.

The single-component compositions according to the invention, which are used as such, that is to say undiluted, or in the form of dispersions in diluents, are stable in storage in the absence of water and cure starting at ambient temperature (after removal of the solvents in the case of dispersions) to form elastomers, in the presence of water.

After the compositions as such have been deposited onto solid substrates, in a moist atmosphere, it is found that a process of curing to elastomers takes place, proceeding from the outside towards the inside of the deposited mass. A surface skin forms first and then the crosslinking continues in depth.

The complete formation of the skin, which manifests itself as a nonsticky surface feel, requires a period of time which can be in the range from 1 minute to 55 minutes; this period depends on the relative humidity content of the atmosphere surrounding the compositions and on the ease of crosslinking of the latter.

Furthermore, the cure in depth of the deposited

layers, which must be sufficient to allow the elastomers formed to be demoulded and handled, requires a longer period of time. This period depends, in fact, not only on the factors mentioned above in the case of the formation of a nonsticky feel, but also on the thickness of the deposited layers, which thickness generally ranges between 0.5 mm and several centimetres. This longer period of time may lie between 10 minutes and 20 hours.

The single-component compositions may be employed for many applications, such as sealing in the building industry, the assembly of a very wide variety of materials (metals, plastics, natural and synthetic rubbers, wood, cardboard, earthenware, brick, ceramic, glass, stone, concrete, masonry components), the insulation of electrical conductors, coating of electronic circuits, and the preparation of moulds used for the manufacture of objects made of synthetic resins or foams.

The abovementioned dispersions of these compositions in the diluents can be employed for thin-layer impregnation of inorganic, synthetic , organic, metallic, woven or nonwoven products and articles, and coating of metal, plastic or cellulosic sheets. The deposition can be produced, for example, by dipping or by spraying; in the latter case, use is made of a spray gun which permits uniform coatings with a thickness of 5 to 300 µm to be obtained. After the spraying of the dispersions, the diluents evaporate off and the compositions released cure to

a rubbery film.

The manufacture of two-component compositions according to the invention is also carried out by mixing the various constituents in suitable equipment. To obtain homogeneous compositions it is preferable to mix the polymers (A) with the fillers (C) first; the combination may be heated for at least 30 minutes to a temperature above 80°C so as to complete the wetting of the fillers by the oils. The other constituents, that is to say the crosslinking agents (B), the organic tin derivative and, if desired, various additives and adjuvants, and even water, can be added to the mixture obtained, which is preferably heated to a temperature below 80°C, for example of the order of ambient temperature.

Such compositions are not stable in storage and they must therefore be employed quickly, for example within a time interval of 40 minutes.

The various additives and adjuvants are the same as those introduced into the single-component compositions. In particular, the α,ω-bis(triorganosiloxy)diorganopolysiloxane polymers with a viscosity of at least 10 mPa s at 25°C, in which the organic radicals linked to the silicon atoms are chosen from methyl, vinyl and phenyl radicals need to be mentioned again. α,ω-(Trimethylsiloxy)dimethylpolysiloxane oils with a viscosity of preferably 20 mPa s at 25°C to 1,000 mPa s at 25°C, are generally employed in a proportion not exceeding 150 parts per

100 parts of polymer (A).

The introduction of water in a proportion not exceeding 1 part per 100 parts of polymers (A) is recommended to promote the curing of the two-component compositions which are employed in thick layers whose thickness is, for example, greater than 2 cm.

This water addition is unnecessary if the fillers (C) contain enough of it. To facilitate its incorporation, water is preferably added in the form of a dispersion in a paste consisting, for example, of the above-mentioned α,ω-bis(triorganosiloxy)diorganopolysiloxane oils and of the fillers (C).

For packaging and storage, the two-component compositions cannot therefore contain all the fundamental constituents, that is to say the polymers (A), the crosslinker (B), the fillers (C) and the tin catalyst (E). On industrial scale, they must be manufactured in the form of two components, each being stable in storage.

A first, storage-stable, component may, for example, comprise the constituents (A), (B) and (C); it is preferably prepared by introducing the crosslinking agents (B) into the homogeneous mixture produced by compounding the polymers (A) with the fillers (C).

The second component then comprises the tin catalyst.

Other ways of presenting the two-component compositions may be chosen; for example, a first component

containing the polymers (A) and the fillers (C), and a second component containing the crosslinking agents (B) and the tin catalyst.

In many applications it is preferable that each of the two components be sufficiently fluid so as to easily form compositions whose viscosity ranges, for example, from 10,000 to 800,000 mPa s at 25°C when mixed.

These compositions, which remain sufficiently fluid for at least 40 minutes, preferably for at least 80 minutes, after the mixing of the two components, can be employed more especially for the manufacture of silicone elastomer moulds; they may, however, be employed for other applications such as coating electronic equipment and coating metallic or textile or cellulosic surfaces.

The moulds which are manufactured are intended to reproduce articles made of cellular or noncellular materials consisting of organic polymers. Among these materials mention may be made of polyurethanes, polyesters, polyamides, and polyvinyl chloride. The use of these moulds for the reproduction of polyurethane articles is, however, recommended, since they stand up well to the attack by constituents of the mixtures used to produce polyurethane materials (in particular polyisocyanates).

The introduction of the tin catalyst according to the invention, at least partly consisting of tin monochelate, makes it possible to attain the best use conditions in the case of the single- and two-component

compositions. It makes it possible subsequently to obtain elastomers with stable use properties and with tensile properties which are stable with time which are independent of the age and of the storage conditions of the compositions.

- EXAMPLE 1:

0.1 mole of dibutyltin oxide, 0.1 mole (20.1 g) of lauric acid, 21.33 g of 1-benzoyl-4-methyl-2-pentanone and 130 ml of cyclohexane are introduced in succession into a 250ml three-necked round-bottomed flask fitted with a central stirrer, a condenser and a thermometer.

The mixture is heated under reflux for 2 hours under a nitrogen atmosphere and then most of the cyclohexane is distilled off until the reaction mass is at 90°C.

100 ml of cyclohexane and 2 ml of water are collected.

The reaction mixture is then concentrated in a rotary evaporator for 30 minutes at 70°C under 0.27 kPa and 65 g of a light-yellow liquid are obtained, containing 53 mol% (calculated in gram-atoms of tin metal) of pentacoordinated tin monochelate, as determined by ^{119}Sn NMR using the abovementioned method described by Peter J. Smith.

- EXAMPLES 2 to 16:

The operating procedure of Example 1 is repeated exactly, except that the reactants and/or the quantities introduced are changed.

The results obtained are collected in Table 1 below.

The reaction may be written schematically as follows:

a R_1R_2SnO + b XH + c CH $\rightleftharpoons$ R_1R_2SnCX + $R_1R_2SnC_2$ + R_1,R_2SnX_2 + H_2O

a, b and c are the molar quantities which are introduced, of R_2SnO, XH and CH, respectively,

XH is the acid introduced,

XH1 : lauric acid,

XH2 : versatic ® acid,

XH3 : $(CH_3)_3CCOOH$ (pivalic) acid,

XH4 : 2-ethylhexanoic acid,

XH5 : acetic acid,

XH6 : benzoic acid,

XH7 : chloroacetic acid,

CH1 : 1-benzoyl-4-methyl-2-pentanone,

CH2 : acetylacetone,

CH3 : dibenzoylmethane,

CH4 : 1,1,1-trifluoro-3-benzoyl acetone.

In Table 1, columns PR1, PR2, PR3 and PR4 give the mol% calculated in gram-atoms of tin metal for the products present in the reaction mixture.

PR1 : R1 R2 Sn CX

PR2 : R1 R2 Sn X2

PR3 : R1 R2 Sn C2

PR4 : X R1 R2 Sn OSn R1 R2 X

TABLE 1

ex.	R1 and R2	a	XH	b	CH	c	PR1	PR2	PR3	PR4
1	C4H9	0,1	XH1	0,1	CH1	0,1	53,0	23,0	17,0	7,0
2	C4H9	0,5	XH1	0,5	CH1	0,5	51,2	22,8	20,3	5,7
3	C4H9	0,2	XH1	0,2	CH1	0,23	54,8	21,0	21,0	2,2
4	C4H9	0,2	XH1	0,23	CH1	0,23	54,0	34,0	12,0	0
5	C4H9	0,05	XH2	0,05	CH1	0,05	56,0	23,0	21,0	0
6	C4H9	0,1	XH3	0,1	CH1	0,1	56,0	20,8	20,0	3,8
7	C4H9	0,1	XH4	0,1	CH1	0,1	51,0	21,4	22,5	5,1
8	C8H17	0,1	XH4	0,1	CH1	0,1	51,1	19,7	23,4	5,8
9	C4H9	0,1	XH5	0,1	CH1	0,1	49,5	18,8	28,2	3,5
10	C4H9	0,1	XH5	0,1	CH2	0,1	75,0	5,8	9,7	9,5
11	C8H17	0,015	XH1	0,015	CH3	0,015	54,5	20,0	16,4	9,1
12	C8H17	0,015	XH1	0,020	CH4	0,020	35,5	44,5	20,0	0
13	C4H9	0,1	XH6	0,1	CH2	0,1	73,0	12,0	6,0	9,0
14	C4H9	0,1	XH6	0,1	CH1	0,1	69,0	12,0	14,0	5,0
15	C8H17	0,1	XH1	0,1	CH1	0,1	61,0	27,0	12,0	0
16	C4H9	0,1	XH7	0,1	CH1	0,1	90,0	4,5	0	5,20

- EXAMPLE 17:

1 mole (360 g) of di-n-octyltin oxide, 1.2 mole (244.8 g) of 1-benzoyl-4-methyl-2-pentanone and 0.9 mole (129 g) of 2-ethylthexanoic acid are charged into a 1-litre three-necked round-bottomed flask fitted with a central stirrer, a condenser and a thermometer.

A clear yellow oil, with the following physico-chemical characteristics is obtained:

viscosity at 25°C : 163 mPa s

relative density at 25°C : 1.081

refractive index at 25°C : 1.521

- EXAMPLES 18 TO 20:

The operations carried out are the same as in Example 16, except that the molar ratios a, b and c of the reactants are varied; the results obtained are collated in Table 2 below, where R1, R2, a, XH, b, CH, C, PR1, PR2, PR3 and PR4 have the same meaning as in Table 1 above

TABLE 2

ex.	R1 and R2	a	XH	b	CH	c	PR1	PR2	PR3	PR4
17	C8H17	1	XH4	0.9	CH1	1,2	30.4	49.0	7.6	12.0
18	C8H17	1	XH4	1.5	CH1	0.6	49.5	15.0	23.4	10.5
19	C8H17	1	XH4	1	CH1	1	44.0	13.0	29.5	13.5
20	C8H17	1	XH4	0.6	CH1	1.5	33.2	7.3	47.7	11.3

- COMPARATIVE EXAMPLE 21 AND EXAMPLES 22 TO 26:

A composition P_1 is prepared by mixing:

- 100 parts of an α,ω-dihydroxydimethylpolysiloxane oil with a viscosity of 10,000 mPa s at 25°C,

- 70 parts of an α,ω-bis(trimethylsiloxy)dimethylpolysiloxane oil with a viscosity of 800 mPa s at 25°C,

- 55 parts of a combustion silica with a specific surface area of 300 m^2/g, treated with hexamethyldisilazane,

- 50 parts of ground quartz with a mean particle diameter of 5 micrometres, and

- 10 parts of a paste made up of 90 parts of the abovementioned α,ω-dihydroxydimethylpolysiloxane oil, with a viscosity of 10,000 mPa s at 25°C, 5 parts of a combustion silica with a specific surface area of 150 m^2/g and 5 parts of water.

The composition P_1 is catalysed with a crosslinking system containing some of the catalysts C forming the subject of the preceding examples and partially hydrolysed ethyl silicate.

The composition P_1 is catalysed by mixing 100 parts of this composition with two parts of the crosslinking system consisting of 17.5% by weight of catalyst C and 82.5% by weight of partially hydrolysed ethyl silicate. This crosslinking system is employed as such, freshly prepared ($\Delta t = 0$) or after having undergone aging at 70°C for a period Δt of 72, 168 and 336 hours.

The spreading time st of the catalysed composition is then determined by noting the time for which this composition remains in a sufficiently fluid state to spread under its own weight and thus to adopt the configuration of the internal volume of the receptacles into which it is poured.

The test employed for assessing the spreadability is as follows:

The freshly catalysed composition (15 grams) is poured into an aluminium capsule of cylindrical shape with a diameter of 4 cm; after a time not exceeding 5 minutes its surface must be perfectly horizontal.

The catalysed composition is converted into a silicone elastomer after several hours at ambient temperature; 24 hours (1 day) and 96 hours (4 days) after the preparation of this catalysed composition the Shore A hardness of the elastomer formed is measured. The results relating to the spreading time (st) in minutes and the Shore A hardness values (SAH1 and SAH4) are collated in Table 3 below.

The catalyst in the comparative example is di-n-octyltin di-2-ethylhexanoate.

The results are collated in Table 3 below, where C ex n shows that the tin catalyst employed is that obtained in Example n.

It is found that the catalysts according to the invention, as distinct from the control catalyst, endow

the silicone elastomer with satisfactory hardness and spreading time values even after prolonged aging of the crosslinking system.

TABLE 3

EXAMPLE		21			22			23		
CATALYST		CONTROL			C ex 8			C ex 17		
		st	SAH1	SAH4	st	SAH1	SAH4	st	SAH1	SAH4
Δt	0	170	16	26	240	12	24	170	15	25
	72	210	12	24				180	16	26
	168	290	6	23	235	13	24	160	14	25
	336	310	5	23	200	17	23	170	15	25

EXAMPLE		24			25			26		
CATALYST		C ex 18			C ex 19			C ex 20		
		st	SAH1	SAH2	st	SAH1	SAH2	st	SAH1	SAH2
Δt	0	170	15	25	240	13	24	150	18	27
	72	170	17	25				170	16	24
	168				235	13	24	180	16	25
	336	230	15	26	200	17	24	200	16	26

- COMPARATIVE EXAMPLE 27 AND EXAMPLE 28:

The operating procedure of the preceding Examples 21 to 26 is repeated, except that the catalyst employed as control in the comparative Example 27 is di(n-octyl)-tin dilaurate and the catalyst in Example 28 is that synthesized in Example 15 above.

The results obtained are collated in Table 4 below.

It is found that the catalyst employed in Example 28, in contrast to the control catalyst in comparative Example 27, endows the silicone elastomer with satisfactory hardness and spreading time values even after prolonged aging.

TABLE 4

EXAMPLE		27			28		
CATALYST		CONTROL			C ex 15		
		st	SAH1	SAH2	st	SAH1	SAH2
Δt	0	160	17	26	95	20	26
	72	195	17	25	95	20	25
	144	100	19	27	100	20	25
	288	90	18	26	100	20	25

- COMPARATIVE EXAMPLE 29 AND EXAMPLES 30 TO 32:

The purpose of these Examples is to demonstrate the better natural aging behaviour of the elastomers obtained from 100 parts of composition P_1 of Example 21 to 26, catalysed with 5 parts of a crosslinking system consisting of 17.5% by weight of catalyst C and 82.5% by weight of partially hydrolysed ethyl silicate.

The catalysed composition is deposited on a polyethylene plaque, in the form of a layer with a thickness of 2mm. After a period of 24 hours at rest in the ambient air the elastomer film obtained is demoulded and is allowed to age at a temperature of 20°C for various times (in months).

The Shore A hardness and the tear resistance TR (expressed in kN/m) of the film which has been subjected to the abovementioned aging times are measured.

The results are collated in Table 5 below, where C ex n shows that the tin catalyst employed is that obtained in Example n. The control catalyst in Comparative Example 29 is di-n-octyltin di-2-ethylhexanoate.

Table 5

EXAMPLE	CATALYST	AGING PERIOD									
		0 MONTHS		1 MONTH		3 MONTHS		7MONTHS		11MONTHS	
	C ex n	SAH	TR	SAH	TR	SAH	TR	SAH	TR	SAH	TR
29	CONTROL	38	25	41	25	42	24	43	15	45	6
30	C ex 18	38	24	40	24	41	24	40	23	43	10
31	C ex 17	35	24	37	21	39	23	38	22	38	23
32	C ex 20	37	24	40	25	41	25	40	23	43	17

From Table 5 it can be seen that the better stability of the elastomer is obtained with a catalyst in accordance with the invention.

- COMPARATIVE EXAMPLE 33 AND EXAMPLE 34:

The following are triturated in a kneader:

- 100 parts of an α,ω-dihydroxydimethylpolysiloxane oil with a viscosity of 70,000 mPa s at 25°C,
- 20 parts of a bis(trimethylsiloxy)dimethylpolysiloxane oil with a viscosity of 100 mPa s at 25°C,
- 130 parts of calcium carbonate with a mean particle diameter of 5 micrometres, and
- 10 parts of combustion silica with a specific surface area of 150 m^2/g.

When the mass is homogeneous, all the solution produced by mixing the following ingredients is added to it:

- 5.5 parts of silane of formula $Si(OCH_2CH_2OC_2H_5)_4$
- 2.5 parts of silane of formula $(CH_3O)_3Si(CH_2)_3NH-CH_2CH_2NH_2$
- 0.040 part of the organic tin derivative which is prepared according to the procedure of Example 16 above.

The single-component composition thus obtained is stored in the absence of moisture in sealed aluminium tubes (Example 34); another composition, identical with the preceding, is prepared, except that the organic tin derivative employed is only dibutyltin dilaurate, and the quantity employed is identical, namely 0.040 part (comparative Example 33).

This composition is also packaged in sealed aluminium tubes. The storage stability of both compositions is checked; for this purpose, the tubes containing them are left for 72 hours in an oven heated to 100°C.

The tubes are allowed to cool and their contents (and the contents of tubes which have not been subjected to a period of heating, and have been stored for a period of 1 month at ambient temperature) are spread in the form of a layer with a thickness of 2 mm, in the open air, on a polytetrafluoroethylene plate. The deposited layer changes into a rubbery film; 24 hours after the deposition of the layer the elastomer film is removed and the tensile properties of the elastomers are measured after aging for 7 days at ambient temperature.

The results are collated in Table 6 below:

TABLE 6

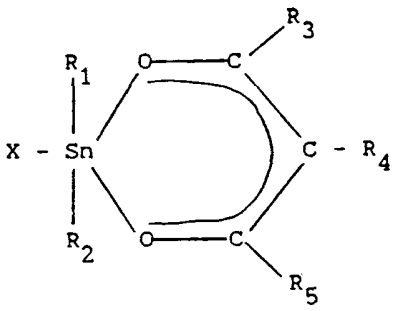
Tensile properties	EXAMPLE 33		EXAMPLE 34	
	Contents of the tubes stored at ambient temperature	Contents of the tubes aged 72 hours at 100°C	Contents of the tubes stored at ambient temperature	Contents of the tubes aged 72 hours at 100°C
Shore A hardness	27	10	26	-
Tensile strength in MPa	1.1	1.0	1.0	-
Elongation at break in %	515	450	348	-

- : not measurable.

Inspection of the values of the tensile properties demonstrates clearly that, in order to retain these properties with time, it is advantageous to employ the catalyst mixture according to the invention rather than di-n-butyltin dilaurate alone.

The claims defining the invention are as follows:

1. A monochelate of pentacoordinated tin of valency IV, of formula:



(1)

in which:

- R_1 and R_2, which are the same or different denote unsubstituted or substituted monovalent C_1-C_{18} organic hydrocarbon radicals,
- R_3 and R_5, which are the same or different, are chosen from radicals R_1 and R_2, hydrogen, C_1-C_5 alkoxy radicals or silyl radicals $Si(R_1)_3$,
- R_4 is hydrogen, an optionally halogenated C_1-C_8 hydrocarbon radical, or R_4 and R_5, together with the carbon atoms to which they are attached, form a divalent C_5-C_{12} cyclic hydrocarbon radical unsubstituted or substituted by chlorine, nitro or cyano, and
- X is a monocarboxylate radical of formula R_6COO in which R_6 has the same meaning as R_1 above.

2. A monochelate according to claim 1 in which R_1 and R_2, which are the same or different, are butyl or n-octyl and X is the monocarboxylate radical of lauric acid,

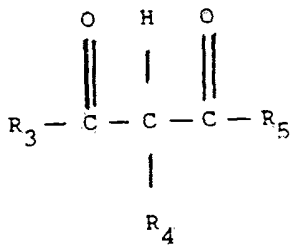
versatic acid, pivalic acid, 2-ethylhexanoic acid, acetic acid, benzoic acid or chloroacetic acid.

3. A monochelate according to claim 1 or 2 in which R_3 and R_5 which are the same or different are methyl, trifluoromethyl, isobutyl or phenyl, and R_4 is hydrogen.

4. Process for the preparation of a tin monochelate of formula (1) defined in any one of claims 1 to 3, which comprises reacting a tin oxide of formula:

$$R_1R_2SnO \qquad (2)$$

with a β-dicarbonyl compound of formula:



(3)

and with an organic acid of formula:

$$XH \qquad (4)$$

in which R_1, R_2, R_3, R_4, R_5 and X have the same definitions as in claim 1, and removing the water formed.

5. Process according to claim 4, in which the molar ratio of compound (3) to compound (4) is between 0.4 and 2.5, and the molar ratio of compound (2) to compounds [(3) & (4)] is between 1/0.8 and 1/3.

6. Process according to claim 4 or 5, in which

the reaction is carried out by mixing the compounds of formulae (2), (3) and (4) in a closed reactor in the absence of atmospheric water, with the removal of water.

7. Process according to claim 4 or 5, in which the compounds of formulae (2) and (4) are first reacted to obtain, after removal of water, the distannoxane of formula:

$$XR_1R_2SnOSnR_1R_2X \qquad (5)$$

and then the distannoxane (5) is reacted with the β-dicarbonyl compound (3) with removal of water.

8. An organopolysiloxane composition comprising a silicone base capable of being cured to a silicone elastomer by a polycondensation reaction starting at ambient temperature and a catalytically effective quantity of a catalyst chosen from a monochelate of formula (1) defined in any one of claims 1 to 3 or the reaction product obtained by using the process of any one of claims 4 to 7.

9. A composition according to claim 8, in which the base comprises:

A. - 100 parts by weight of an α,ω-dihydroxypolydiorganosiloxane polymer with a viscosity of 500 to 1,000,000 mPa s at 25°C, consisting of a succession of $(R_2)SiO$ units where the symbols R, which are identical or different, denote hydrocarbon radicals of from 1 to 10 carbon atoms, unsubstituted or substituted by halogen atoms or cyano groups,

B. - 0.5 to 20 parts by weight of a crosslinking agent in the form of an organosilicon compound bearing, per molecule, more than two hydrolysable groups linked to silicon,

C. - 0 to 250 parts by weight of inorganic filler, and

D. - 0 to 20 parts by weight of an adhesion promoter.

10. Composition according to claim 8 or 9, characterized in that the crosslinking agent (B) is a silane of formula:

$$R_aSi(Z)_{4-a} \qquad (6)$$

in which R is a hydrocarbon radical of from 1 to 10 carbon atoms and Z is N-substituted amino, N-substituted amido, N,N-disubstituted aminoxy, ketiminoxy, alkoxy, alkoxyalkylenoxy, enoxy or acyloxy groups and a is 0 or 1.

11. A compound according to claim 1 substantially as described in any one of Examples 1 to 20.

12. A composition according to any one of claims 8 to 10 substantially as described in any one of Examples 22-26, 28, 30-32 and 34.

13. The cured product of a composition as claimed in any one of claims 8 to 10 or 12.

Dated this 28th day of December, 1990

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