12113/88

596500

COMMONWEALTH of AUSTRALIA

PATENTS ACT 1952

APPLICATION FOR A STANDARD PATENT

~~I~~ We

RHONE-POULENC CHIMIE,
of 25 Quai Paul Doumer, 92408 COURBEVOIE,
FRANCE

APPLICATION ACCEPTED AND AMENDMENTS
ALLOWED 23-2-90

hereby apply for the grant of a Standard Patent for an invention entitled:

"SILICONE ELASTOMER POLYCONDENSATION COMPOSITION CONTAINING IODINE"

which is described in the accompanying ~~provisional~~ complete specification.

Details of basic application(s):—

Number	Convention Country	Date
8702883	FRANCE	26th February 1987

LODGED AT SUB-OFFICE
24 FEB 1988
Melbourne

The address for service is care of DAVIES & COLLISON, Patent Attorneys, of 1 Little Collins Street, Melbourne, in the State of Victoria, Commonwealth of Australia.

Dated this 24th day of February 1988

To: THE COMMISSIONER OF PATENTS

H. W. Rimington
(a member of the firm of DAVIES & COLLISON for and on behalf of the Applicant).

Davies & Collison, Melbourne and Canberra.

COMMONWEALTH OF AUSTRALIA

PATENTS ACT 1952–1973

DECLARATION IN SUPPORT OF CONVENTION OR NON–CONVENTION APPLICATION FOR A PATENT OR PATENT OF ADDITION

Insert title of invention.

In support of the Application made for a patent ~~patent of addition~~ for an invention entitled: "SILICONE ELASTOMER POLYCONDENSATION COMPOSITION CONTAINING IODINE"

Insert full name(s) and address(es) of declarant(s) being the applicant(s) or person(s) authorized to sign on behalf of an applicant company.

I Jean-Louis SEUGNET,
~~We~~ of: RHONE-POULENC CHIMIE, a French Body Corporate of: 25, Quai Paul Doumer, 92408 COURBEVOIE, France.

Cross out whichever of paragraphs 1(a) or 1(b) does not apply
1(a) relates to application made by individual(s)
1(b) relates to application made by company; insert name of applicant company.

do solemnly and sincerely declare as follows :–

~~1. (a) I am / We are the applicant for the patent / patent of addition~~

or (b) I am authorized by
RHONE-POULENC CHIMIE,

the applicant ~~s~~ for the patent ~~patent of addition~~ to make this declaration on its ~~their~~ behalf.

Cross out whichever of paragraphs 2(a) or 2(b) does not apply
2(a) relates to application made by inventor(s)
2(b) relates to application made by company(s) or person(s) who are not inventor(s); insert full name(s) and address(es) of inventors.

2. (a) ~~I am / We are~~ the actual inventor of the invention

or (b) GUY CYPRIEN: of: 7, rue d'Anjou, 92240 L'HAY LES ROSES, France: ALAIN FISCH, of: 22, rue de l'Yvette, 75016 PARIS, France: JOHNNY HAGGIAGE, of: 72, rue du Fort Saint-irenee, 69005 LYON, France: HUGUES PORTE, of: 6, chemin de Crepieux, 69300 CALUIRE, France; THIERRY PRAZUCK, of: 53 avenue Mathurin Moreau, 75019 PARIS, France and GHISLAINE TORRES, of: 104, rue Ney, 69006 LYON France.
All citizens of France.

~~is~~ are the actual inventor S of the invention and the facts upon which the applicant ~~s~~ is ~~is~~ ~~are~~ entitled to make the application are as follows :–

State manner in which applicant(s) derive title from inventor(s)

"The applicant would if a patent were granted upon an application made by the inventors, be entitled to have the patent assigned to it".

Cross out paragraphs 3 and 4 for non-convention applications. For convention applications, insert basic country(s) followed by date(s) and basic applicant(s).

3. The basic application as defined by Section 141 of the Act was ~~were~~ made
in FRANCE: No. 87/02 883 on the 26th February, 1987
by RHONE-POULENC CHIMIE
in .... on the ....
by ....
in .... on the ....
by ....

4. The basic application referred to in paragraph 3 of this Declaration was ~~were~~ the first application made in a Convention country in respect of the invention the subject of the application.

Insert place and date of signature.

Declared at St-Fons this 12 day of January 1988

RHONE-POULENC CH...
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Signature of declarant(s) (no attestation required)

Note: Initial all alterations.

Jean-Louis SEUGNET
Ingénieur-Brevets

(12) PATENT ABRIDGMENT **(11)** Document No. **AU-B-12113/88**
(19) AUSTRALIAN PATENT OFFICE **(10)** Acceptance No. **596500**

(54) Title
SILICONE ELASTOMER POLYCONDENSATION COMPOSITION CONTAINING IODINE

International Patent Classification(s)

(51)^4	**C08G 077/38**	**A61K 033/18**	**A61K 047/00**	**C08G 077/04**
	C08G 077/44	**C08K 003/16**	**C08K 003/24**	**C08K 005/00**
	C08K 005/09	**C08K 005/54**	**C08K 013/02**	**C08L 083/04**

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87 02883	**26.02.87**	**FR FRANCE**

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(56) Prior Art Documents
AU 12115/88 C08G 77/44, 81/00 C08L 83/04
AU 12114/88 C08L 83/04 C08G 77/38
AU 12112/88 C08G 77/44 81/00 C08L 83/04

(57) Claim

1. A diorganopolysiloxane composition which is capable of being cured to a silicone elastomer by a polycondensation reaction, and which comprises:

(A) : at least one diorganopolysiloxane oil carrying at each end of the chain at least two condensable or hydrolysable groups, or a single hydroxyl group,

(B) : from 5 to 130 parts by weight per 100 parts by weight of (A) of an organic and/or inorganic iodine compound, in liquid or solid form at ambient temperature, soluble in water, nontoxic and not inhibiting the cure of the composition to an elastomer,

(C) : a catalyst of polycondensation of the oil, and, when (A) is an oil with hydroxyl end groups,

(D) : a silane containing at least three condensable or hydrolysable groups.

16. A composition according to any one of the preceding claims, cured to an elastomer.

17. A water treatment process in which an elastomer as defined in claim 16 is immersed in water to release a continuous and controlled quantity of iodine into the water.

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FORM 10

COMMONWEALTH OF AUSTRALIA

PATENTS ACT 1952-1973

COMPLETE SPECIFICATION

(ORIGINAL)

FOR OFFICE USE:

CLASS INT. CLASS

APPLICATION NUMBER:
LODGED:

COMPLETE SPECIFICATION LODGED:
ACCEPTED:
PUBLISHED:

PRIORITY:

RELATED ART:

This document contains the amendments made under Section 49 and is correct for printing.

NAME OF APPLICANT: RHONE-POULENC CHIMIE

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COMPLETE SPECIFICATION FOR THE INVENTION ENTITLED:

SILICONE ELASTOMER POLYCONDENSATION COMPOSITION CONTAINING IODINE

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

The present invention relates to a silicone elastomer composition containing iodine, useful for iodising water for domestic use.

The number of people suffering from iodine deficiency is currently estimated at several hundred million worldwide. The geographical regions affected to the greatest degree are Latin America, particularly along the Andean Cordillera, and virtually all the noncoastal regions of Africa and of Asia (Pakistan, India, Nepal, China, Laos, and so on).

The main pathological consequences of iodine deficiency are well known. These are essentially, on the one hand, goitre and its complications among which may be included swallowing disorders, respiratory disorders, cancerization and peripheral circulation disorders and, on the other hand, hypothyroidism and its complications, among which may be mentioned: cretinism, cerebral disorders, premature births, miscarriages and congenital abnormalities.

While iodine deficiency has disappeared from industrialized countries because of the iodization or iodination of cooking salt, this is not the case in the developing countries, where the two main compaigns undertaken so far have remained ineffective.

These campaigns have been essentially aimed at, on the one hand:

- the iodization of cooking salt: this does not work in the majority of the developing countries because very frequently the consumption of salt is minimal, the systems for the distribution of salt via the economic and commercial networks are virtually nonexistent and, finally, in a tropical region, iodine which is added to salt escapes rapidly from it if it is not perfectly packaged;

and, on the other hand;

- the intramuscular injection of iodinated oil: such injections have the advantage of exhibiting a delayed action, but are not devoid of disadvantages, particularly the risks of infection, the risks of iodine allergy, and the risks of hyperthyroidism or of hypothyroidism, which are caused by the injection of a necessarily supraphysiological dosage.

Furthermore, Belgian Patent BE-A-889,680 describes the introduction of oligoelements, including iodine, into the drinking water of ruminants, in the form of a dispersion in a binder such as, for example, plaster of Paris. A diorganopolysiloxane may be added with a view to slowing down the diffusion of the oligoelement. In addition, the use of iodine and of iodine compounds for disinfecting or for purifying water is well known. US Patents US-A-2,347,567, US-A-2,743,208 and US-A-3,408,295 may be mentioned by way of example.

There are also in existence very many patents describing the use of polymeric systems, especially using a silicone, for the controlled release of an active ingredient, for example by means of a transdermic system (US Patent US-A-4,053,580), or by oral injection, especially for ruminants (French Patent FR-A-2,560,768).

Lastly, US Patent US-A-4,384,960 describes the placing of iodine (I_2) tablets in a plastic bottle into which water enters through a membrane. The water dissolves the iodine. The purpose of the membrane is merely to prevent the iodine tablets leaving the bottle. It is suggested, furthermore, that it is possible to introduce the iodine into the bottle in a liquid dispersion of silicone or of a dimethylsiloxane elastomer, and then to cure them. However this suggested solution is not technically feasible because I_2 is a well known inhibitor of catalysts for curing silicone elastomers capable of being vulcanized at ambient temperature (see, in particular, the publication by W.D. Morain et al., Plastic and Reconstructive Surgery 59, 2, 215-222 (1977)).

Furthermore, in the system of patent US-A-4,384,960, there is no control of the release of iodine and the iodization of water takes place by noncontinuous or continuous addition of a few drops of highly iodinated (to saturation) water contained in the bottle, to any receptacle containing untreated water. It is clear that the solution proposed by US-A-4,384,960 is imperfect, especially because it involves an individual method which, like the intramuscular injection of iodine, requires mass education and mobilization of populations.

The present invention provides a new composition capable of being cured to give silicone elastomer polycondensation compositions containing iodine capable of being employed for the continuous treatment of water for domestic use, particularly in water supply systems and for treatment of water in wells and boreholes. This makes it possible to distribute (release) a controlled and adapted quantity of iodine with a view to ensuring the eradication of the various diseases caused by iodine deficiency.

These silicone elastomer polycondensation compositions contain iodine and when suitably immersed in places containing water to be treated, especially wells and boreholes, continually distribute (release), preferably for at least a year, an appropriate quanitity of iodine in a therapeutically active and effective form and dosage in order to treat the various diseases caused by iodine deficiency.

These compositions have no undesirable secondary action which is detrimental to the water to be treated from a chemical or biological standpoint.

The silicone elastomer polycondensation compositions containing iodine are adapted to the environment in which the water to be treated is to be found, and are particularly well adapted to use in wells and/or boreholes and can be easily replaced.

The iodine compound used in the compositions does not inhibit the cure (crosslinking) of the polycondensation silicone composition to an elastomer.

The present invention provides a diorganopolysiloxane composition which is capable of being cured to a silicone elastomer by a polycondensation reaction and which comprises:

(A) at least one diorganopolysiloxane oil carrying at each end of the chain at least two condensable or hydrolysable groups, or a single hydroxyl group,

(B) from 5 to 130 parts by weight per 100 parts by weight of (A) of at least one organic and/or inorganic iodine compound in solid or liquid form at ambient temperature, soluble in water, nontoxic and which does not inhibit the cure of the composition to an elastomer,

(C) a catalyst for polycondensation of the oil, and when (A) is an oil with hydroxyl end groups,

(D) a silane containing at least three condensable or hydrolysable groups.

Preferably from 10 to 100 parts of iodine compound

(B) per 100 parts of the oil (A) are present.

Unless stated otherwise, all percentages and parts are by weight.

The inorganic iodine compound may be:

- an iodide or iodate of general formula:

$(M^{a+})(I^-)a$

or $(M^{a+})(IO_3^-)a$

in which a is an integer greater than or equal to 1 and M is a cation of an alkali metal such as sodium or potassium, an alkaline-earth metal such as magnesium or calcium, a transition metal such as iron or manganese, an ammonium cation $(NZ_4)^+$, in which the radicals Z, which may be identical or different, each denote a linear or branched C_1-C_{20} alkyl radical or a hydrogen atom, such as the ammonium ion NH_4^+.

The cations M^{a+} and NZ_4^+ are chosen so that the corresponding iodide or iodate is a solid or a liquid at ambient temperature, is soluble in water and is nontoxic.

The iodides and iodates which may be employed are particularly those of formulae:

NaI, $NaIO_3$,

KI, KIO_3,

MgI_2, $MgI_2 . 8H_2O$,

$Mg(IO_3)_2 . 4H_2O$,

NH_4I

$FeI_2.4H_2O$

MnI_2

These salts may contain water of hydration or water of formation.

As a compound of iodine which is at the same time organic and inorganic, use may be made, for example, of calcium iodobehenate of formula:

$$(C_{21}H_{42}ICO_2)Ca$$

Iodinated polyvinylpyrrolidone may be mentioned as an organic iodine compound.

For reasons of ease of use, solid iodine compounds are preferred, and NaI and KIO_3 are the most preferred among these.

All the iodine compounds such as defined above release iodine in a nontoxic and therapeutically effective form when they are dissolved in the water to be treated. A nontoxic iodine compound means according to the invention a compound which, in solution, is not toxic in the dosages recommended by the present invention.

A water-soluble iodine compound means a compound having a solubility of at least 100 µg/l at ambient temperature.

Furthermore the iodine compounds must not inhibit the cure of the silicone composition to an elastomer. Molecular iodine I_2 is therefore excluded from the iodine compounds capable of being employed within the scope of the present invention.

In the developing countries in particular, water for domestic use (drinking, washing, irrigation, and the like) is essentially provided by structures of two types, wells and boreholes.

For obvious reasons of cost, efficiency and salubriousness, the new creation of a water point is frequently produced by drilling.

A borehole is a column of air drilled through compact rocks having a depth which is generally between 20 and 100 metres and a diameter of at least approximately 10 cm. Water filters into this column through cracks or various interstices. The water reserve which is immediately available thus consists of a column of 10 to 70 metres, generally from 30 to 50 metres, in height, which is withdrawn with the aid of an immersed-body pump.

This water is renewed chiefly as a function of the use of the borehole, which depends on the season. In fact, in the rainy season the borehole is traditionally used less. On the other hand, in the dry season the borehole runs for approximately 12 hours daily, which is a quantity of between 5 and 10 m^3 per day for approximately six months.

As a general rule, a well may be run dry twice daily at the time of the dry season, which corresponds to a maximum usage of 5 to 10 m^3, based on these average statistical data.

Numerous studies show that in the regions in which goitre is highly endemic, the preexisting proportions of iodine equivalent in the water in boreholes or in wells is less than 2 micrograms per litre (2 µg/l). It is currently estimated that a daily input of approximately 100 µg of iodine equivalent per day per person would be sufficient to prevent the development of endemic goitre and probably approximately 150 µg in the presence of regular consumption of goitrogenic substances. Conversely, an acute iodine intoxication may be responsible for neurological irritation, for hyperthyroidism or for hypothyroidism.

It is assumed in medical practice that the ingestion of a dose of 3 grams of iodine equivalent by an adult subject as a single dose does not produce any secondary effect.

Consequently, the objective sought after is to make it possible to provide an individual with 20 to 200 µg, preferably approximately 100 µg, of iodine equivalent daily.

Thus, with the knowledge that, on average, an adult individual ingests 2 litres of water daily and on the basis of the above data (a borehole with an output of 600 l/h), it appears desirable that a litre of treated water should contain approximately 50 µg/l of iodine, which corresponds to 50 µg of iodine equivalent per litre per person, which requires the silicone composition to release 720 mg/d of iodine equivalent, i.e. 270 g of iodine equivalent to be released over a year.

Surprisingly and unexpectedly, it has been found that it is possible to include in a silicone elastomer polycondensation composition large quantities of iodine compound in a solid or liquid form such as defined above, namely from 5 to 130 parts, preferably from 10 to 100 per 100 parts of the total of the diorganopolysiloxane oil (A), optionally filled with a reinforcing or semireinforcing siliceous filler beforehand, and thus to obtain a crosslinked elastomer which has the required mechanical characteristics for the intended application and which makes it possible to ensure a continuous and controlled release of iodine, preferably for at least a year, when immersed in water.

The controlled iodine release system forms part of the matrix systems in which the diffusion of the active ingredient is normally determined by Fick's Law, that is to say by diffusion kinetics of the order of 1/2 for only 60% by weight of the active ingredient. Beyond 60% the matrix is exhausted and the diffusion fluxes are greatly reduced. Surprisingly and unexpectedly, it has been found that the silicone matrix system produced from the present composition releases iodine according to zero-order kinetics and continuously and does so until 80% by weight and more of the iodine compound has been released.

The considerable advantage contributed by the silicone matrix is therefore that it is very easy to extrapolate the continuous diffusion of the active ingredient after a measurement of the quantity released after at least one month, because it is known that the diffusion kinetics are of zero order and that at least 80% of the iodine compound will be released according to these kinetics.

In order to gain complete control of the release of the active ingredient it is advantageous to present the silicone matrix in the form of elementary modules (elements) of various shapes such as cubes, right parallelepipeds, cylinders and spheres, whose fundamental parameters are the following:

- the nature of the iodine compound,
- the mean diameter (particle size) g of the particles of the iodine compound in the preferred case where the latter is a solid,
- the concentration t of the iodine compound within the matrix,
- the surface/volume ratio R of the module.

The nature of the iodine compound and its particle size define the rate of diffusion of the active ingredient through the matrix.

The lower the value of g, the slower v is and vice versa.

The higher the value of t, the greater the flux of active ingredient and vice versa.

The higher the value of R, the greater the high flux of active ingredient and vice versa.

The specialist, using routine experiments, is capable of rapidly and without difficulty obtaining the required result by extrapolating the theoretical elution time which will correspond to the actual time of diffusion of the active ingredient.

In the case of NaI and KIO_3, which are the preferred iodine compounds, g, t and R may be advantageously chosen within the following ranges:

- g of between 1 and 300 µm,
- t of between 10 and 100 parts by weight of iodine compound per 100 parts of (A), and
- R of between 0.5 and 50 in the case of a cylindrical shape.

It is desirable, furthermore, that the iodine compound should be dispersed homogeneously within the matrix.

The diorganopolysiloxane oils (A) capable of being employed in the compositions according to the invention are more particularly those corresponding to the formula (1):

$$Y_nSi_{3-n}O(SiR_2O)_x\,SiR_{3-n}Y_n \qquad (1)$$

in which:

R denotes identical or different monovalent hydrocarbon

radicals, Y denotes identical or different hydrolysable or condensable groups or hydroxy groups,
n is chosen from 1, 2 and 3 with n = 1 when Y is a hydroxyl and x is an integer greater than 1, preferably greater than 10.

The viscosity of the oils of formula (1) is between 50 and 10^6 mPa s at 25°C. As examples of radicals R there may be mentioned alkyl radicals containing from 1 to 8 carbon atoms such as methyl, ethyl, propyl, butyl, hexyl and octyl radicals, vinyl radicals, and phenyl radicals. As examples of substituted radicals R there may be mentioned 3,3,3-trifluoropropyl, chlorophenyl and beta-cyanoethyl radicals.

In the products of formula (1) which are generally employed industrially, at least 60%, on a numerical basis, of the radicals R are methyl radicals, the other radicals being generally phenyl and/or vinyl radicals.

As example of hydrolysable group Y there may be mentioned the amino, acylamino, aminoxy, ketiminoxy, iminoxy, enoxy, alkoxy, alkoxyalkyleneoxy, acyloxy and phosphato groups.

As examples of amino Y groups there may be mentioned n-butylamino, sec-butylamino and cyclohexylamino groups; as those of N-substituted acylamino groups there may be mentioned the benzoylamino group; as those of aminoxy groups, the dimethylaminoxy, diethylaminoxy, dioctylaminoxy and diphenylaminoxy groups; as examples of iminoxy and ketiminoxy Y groups, those derived from acetophenone oxime, acetone oxime, benzophenone oxime, methyl ethyl ketoxime, diisopropyl ketoxime and chlorocyclohexanone oxime.

As alkoxy Y groups there may be mentioned the groups containing from 1 to 8 carbon atoms such as methoxy, ethoxy, propoxy, isopropoxy, butoxy, hexyloxy and octyloxy groups; as an alkoxyalkyleneoxy Y group there may be mentioned the methoxyethyleneoxy group.

As acyloxy Y groups there may be mentioned the groups containing from 1 to 8 carbon atoms such as the formyloxy, acetoxy, propionyloxy and 2-ethylhexanoyloxy groups.

As phosphato Y groups there may be mentioned those derived from dimethyl phosphate, diethyl phosphate and dibutyl phosphate.

As condensable Y groups there may be mentioned hydrogen atoms and halogen atoms, preferably chlorine.

When the groups Y in the formula (1) above are hydroxyl groups, n is then equal to 1, and in order to prepare polyorganosiloxane elastomers from polymers of formula (1) above, it is necessary to employ, in addition to condensation catalysts, crosslinking agents (D), already indicated, which are silanes of general formula:

$$R_{4-a}SiY'_a \qquad (2)$$

in which R has the meanings given above in formula (1) and Y' denotes identical or different hydrolysable or

condensable groups, and
a is equal to 3 or 4.

The examples given in the case of groups Y are applicable to groups Y'.

It is desirable to employ silanes of formula (2) even in the case where Y in the oil (A) is not a hydroxyl group.

In this case, it is desirable to employ groups Y in the oil (A) which are identical with Y' in the silane (D).

The alpha,omega-dihydroxylated diorganopolysiloxanes of formula (1) are generally oils whose viscosity varies from 500 mPa s at 25°C to 500,000 mPa s at 25°C preferably 800 mPa s to 400,000 at 25°C; they are linear polymers consisting essentially of diorganosiloxy units of formula (R_2SiO). However, the presence of other units, generally present as impurities, such as $RSiO_{3/2}$, $RSiO_{1/2}$ and $SiO_{4/2}$ is not ruled out in the proportion not exceeding 1% based on the number of diorganosiloxy units.

The organic radicals linked to the silicon atoms of the base oils and denoted by the symbol R may be chosen from alkyl radicals containing from 1 to 3 carbon atoms such as methyl, ethyl and n-propyl radicals, the vinyl radical, the phenyl radical, the 3,3,3-trifluoropropyl radical and the beta-cyanoethyl radical.

At least 60% of the total of the radicals R are methyl radicals, not more than 1% are vinyl radicals.

By way of illustration of the units denoted by the formula R_2SiO there may be mentioned those of formulae: $(CH_3)_2SiO$, $CH_3(CH_2{=}CH)SiO$, $CH_3(C_6H_5)SiO$, $CF_3CH_2CH_2(CH_3)SiO$, $NC{-}CH_2CH_2(CH_3)SiO$, $NC{-}CH_2(C_6H_5)SiO$.

These base oils are, for the most part, marketed by the silicone manufacturers. Furthermore, their methods of manufacture are well known and can be found described, for example, in French Patents FR-A-1,134,005, FR-A-1,198,749 and FR-A-1,226,745.

As examples of monomeric silanes (D) of formula (2) there may be mentioned more particularly polyacyloxysilanes, polyalkoxysilanes, polyketiminoxysilanes and polyiminoxysilanes and, in particular, the following silanes: $CH_3Si(OCOCH_3)_3$, $C_2H_5Si(OCOCH_3)_3$, $CH_2{=}CHSi(OCOCH_3)_3$, $C_6H_5Si(OCOCH_3)_3$, $CF_3CH_2CH_2Si(OCOCH_3)_3$, $NC{-}CH_2CH_2Si(OCOCH_3)_3$, $CH_2ClSi(OCOCH_2CH_3)_3$, $CH_3Si(ON{=}C(CH_3)C_2H_5)_2OCH_2CH_2OCH_3$, $CH_3Si(ON{=}CH{-}CH_3)_2OCH_2CH_2OCH_3$.

The above silanes (D) associated with alpha,omega-dihydroxylated polydiorganosiloxanes of formula (1) may be employed in single-component compositions which are stable in the absence of air.

As examples of a monomeric silane of formula (2) which, when associated with alpha,omega-dihydroxylated polydiorganosiloxanes of formula (1), may be advantageously employed in two-component compositions, polyalkoxysilanes may be mentioned, and particularly those of formulae: $Si(OC_2H_5)_4$, $Si(O{-}n{-}C_3H_7)_4$, $Si(O{-}isoC_3H_7)_4$, $Si(OC_2H_4OCH_3)_4$,

$CH_3Si(OCH_3)_3$, $CH_2{=}CHSi(OCH_3)_3$, $CH_3Si(OC_2H_4OCH_3)_3$, $ClCH_2Si(OC_2H_5)_3$, $CH_2{=}CHSi(OC_2H_4OCH_3)_3$.

All or part of the monomeric silanes described above may be replaced by polyalkoxypolysiloxanes in which each molecule contains at least two, preferably three Y' atoms and the remaining valencies of silicon are satisfied by siloxane bonds SiO- and SiR. Ethyl polysilicate may be mentioned as an example of polymeric crosslinking agents.

From 0.1 to 20 parts by weight of crosslinking agent of formula (2) are generally employed per 100 parts by weight of polymer of formula (1).

The polyorganosiloxane compositions capable of being cured to an elastomer of the type described above contain from 0.001 to 10 parts by weight, preferably from 0.05 to 3 parts by weight of condensation catalyst (C) per 100 parts by weight of polysiloxane of formula (1).

The content of condensation catalyst in the single-component compositions is generally much lower than that employed in the two-component compositions and is generally between 0.001 and 0.05 part by weight per 100 parts by weight of polysiloxane of formula (2).

Whether they be employed for the preparation of single-component or two-component compositions, the crosslinking agents (D) of formula (2) are products which are available on the silicone market; furthermore, their use in compositions which cure from ambient temperature upwards is known; it appears particularly in French Patents FR-A-1,126,411, FR-A-1,179,969, FR-A-1,189,216, FR-A-1,198,749, FR-A-1,248,826, FR-A-1,314,649, FR-A-1,423,477, FR-A-1,432,799 and FR-A-2,067,636.

The compositions according to the invention may additionally contain reinforcing or semireinforcing or extending fillers (E) which are preferably chosen from siliceous fillers, combustion silicas and precipitated silicas. Preferably they have a specific surface area, measured according to the BET methods, of at least 50 m^2/g, more preferably greater than 70 m^2/g, a mean primary particle size of less than 0.1 µm (micrometre) and an apparent density of less than 200 g/litre.

These silicas may be incorporated preferably as such or after they have been treated with the organosilicon compounds which are usually employed for this purpose. These compounds include methylpolysiloxanes such as hexamethyldisiloxane and octamethylcyclotetrasiloxane, methylpolysilazanes such as hexamethyldisilazane and hexamethylcyclotrisilazane, chlorosilanes such as dimethyldichlorosilane, trimethylchlorosilane, methylvinyldichlorosilane and dimethylvinylchlorosilane, and alkoxysilanes such as dimethyldimethoxysilane, dimethylvinylethoxysilane and trimethylmethoxysilane. In the course of this treatment, the silicas may increase in their initial weight up to a proportion of 20%, preferably approximately 18%.

The semireinforcing or extending fillers have a particle diameter greater than 0.1 μm and are chosen from ground quartz, calcined clays and diatomaceous earths.

From 0 to 100 parts, preferably from 5 to 50 parts, of filler (E) may generally be employed per 100 parts of oil (A).

The components (A), (C) and, if present, (D) which form the basis for the silicone composition are well known to the specialist. They are described in detail in the literature, particularly in many patents, and the majority are commercially available.

Compositions of (A), (C) and, if present, (D) crosslink at ambient temperature in the presence of moisture contributed by atmospheric moisture and/or present in the composition. They may be divided into two large classes. The first class consists of single-component or single-pack compositions which are stable in storage in the absence of atmospheric moisture and which cure to an elastomer in the presence of atmospheric moisture. In this case the condensation catalyst (C) employed is a metal compound, generally a tin, titanium or zirconium compound.

According to the nature of the condensable or hydrolysable groups, these single-component compositions are referred to as acidic, neutral or basic.

As acidic compositions it is possible to employ, for example, the compositions described in patents US-A-3,035,016, US-A-3,077,465, US-A-3,133,891, US-A-3,409,573, US-A-3,438,930, US-A-3,647,917 and US-A-3,886,118.

As neutral compositions it is possible to employ, for example, the compositions described in patents US-A-3,065,194, US-A-3,542,901, US-A-3,689,454, US-A-3,779,986, GB-A-2,052,540, US-A-4,417,042 and EP-A-69,256.

As basic compositions it is possible to employ, for example, the compositions described in patents US-A-3,378,520, US-A-3,364,160, US-A-3,417,047, US-A-3,464,951, US-A-3,742,004 and US-A-3,758,441.

According to a preferred alternative form, it is also possible to employ single-component flowing compositions such as those described in patents US-A-3,922,246, US-A-3,965,280 and US-A-4,143,088.

The second class is the preferred class within the scope of the present invention and consists of the two-component or two-pack compositions, generally containing an alpha,omega-dihydroxydiorganopolysiloxane oil (A), a silane (D) or a product originating from the partial hydrolysis of this silane, and a catalyst (C) which is a metal compound, preferably a tin compound and/or an amine.

Examples of such compositions are described in patents US-A-3,678,002, US-A-3,888,815, US-A-3,933,729, US-A-4,064,096 and GB-A-2,032,936.

Among these compositions, those more particularly preferred are the two-component compositions containing:

(A) : 100 parts of an alpha,omega-dihydroxyorganopolysiloxane oil with a viscosity of 50 to 300,000 mPa s in which the organic radicals are chosen from methyl, ethyl, vinyl, phenyl and 3,3,3-trifluoropropyl radicals, at least 60% of their number being methyl radicals, up to 20% of their number being phenyl radicals, and not more than 2% being vinyl radicals,

(B) : 10 to 130 parts of an iodine compound,

(C) : 0.01 to 1 part (calculated as the weight of tin metal) of a catalytic tin compound,

(D) : 0.5 to 15 parts of a polyalkoxysilane or a polyalkoxysiloxane, and

(E) : 0 to 100 parts, preferably 5 to 50 parts, of siliceous inorganic filler.

The tin catalysts (C) are described copiously in the literature referred to above; in particular, this may be a tin salt of a mono- or dicarboxylic acid. These tin carboxylates are described particularly in the work by Noll (Chemistry and Technology of Silicones, page 337, Academic Press, 1968, 2nd edition). Dibutyltin naphthenate, octanoate, oleate, butyrate and dilaurate, and dibutyltin diacetate may be mentioned in particular.

The product of reaction of a tin salt, especially of a tin dicarboxylate, with ethyl polysilicate, as described in patent US-A-3,186,963, may also be employed as a catalytic tin compound. The product of reaction of a dialkyldialkoxysilane with a tin carboxylate, as described in patent US-A-3,862,919, may also be employed.

The product of reaction of an alkyl silicate or of an alkyltrialkoxysilane with dibutyltin diacetate, as described in Belgium Patent BE-A-842,305 may also be employed.

Among the crosslinking agents (D) those more particularly preferred are the alkyltrialkoxysilanes, alkyl silicates and alkyl polysilicates in which the organic radicals are alkyl radicals containing from 1 to 4 carbon atoms.

The alkyl silicates may be chosen from methyl silicate, ethyl silicate, isopropyl silicate, n-propyl silicate and the polysilicates chosen from the products of partial hydrolysis of these silicates; these are polymers consisting of a high proportion of units of formula $(R^4O)_3SiO_{0.5}$, $R^4OSiO_{1.5}$, $(R^4O)_2SiO$ and SiO_2; the symbol R^4 denoting the methyl, ethyl, isopropyl or n-propyl radicals. They are usually characterized on the basis of their silica content which is established by determining the product of complete hydrolysis of a sample.

The polysilicate employed may be, in particular a partially hydrolysed ethyl silicate marketed under the trademark "Ethyl Silicate-40"^{R} by Union Carbide Corporation, or a partially hydrolysed propyl silicate.

The compositions according to the invention may be extruded or moulded into a variety of shapes, for example in the shape of unit modules (elements) and may then be cured at ambient temperature to an elastomer in contact with atmospheric moisture or by the addition of water. A slight heating to a temperature of 20 to 150°C may accelerate the cure.

The variously shaped elastomer modules (elements) may be kept immersed in the water to be treated according to a quantity (a weight of elastomer) such that the elastomer ensures a continuous and controlled release of iodine, preferably for at least a year. At the end of this period the modules (elements) are replaced.

Surprisingly, it has been found that these cross-linked silicone compositions have sufficient physical characteristics for the intended applications.

The following examples illustrate the invention.

Example 1

A dough is prepared by kneading:

75 parts of alpha,omega-dihydroxymethylpolysiloxane oil with a viscosity of 15,000 mPa s at 25°C,

22.2 parts of celite (diatomaceous earth),

2.3 parts of n-propyl silicate, and

0.5 part of a hydrated dough (mixture of dimethyl polysiloxane oil and combustion silica) containing 5% of water.

The mixture is homogenized for 4 hours and is then filtered.

25 parts of NaI with a mean particle size of 5 µm are added to 100 parts of this dough.

A flowing product is obtained, which is catalysed by the addition of 0.5 g of tin 2-ethylhexanoate.

The product is poured into moulds made of steel covered with an antiadhesive agent (Melinex), of cylindrical shape (diameter equal to 10 mm).

After 1 hour at 100°C a well-crosslinked product is obtained, which has the sufficient mechanical properties for the intended applications.

Experimental protocol for measuring the elution kinetics.

The elastomeric composition containing NaI is cut to the desired length (20 mm), in accordance with the surface/volume ratio (4.80 cm^{-1}) which it is desired to obtain and is immersed in a container of 600 ml of distilled water, thermostated at 20°C.

The container is equipped with a magnetic stirring system driven in a slow rotary motion (100 rev/min) ensuring the homogeneity of the solution. It is covered with a lid in order to reduce water evaporation to a minimum.

1-ml samples are taken daily during the initial period of elution, and weekly after a fortnight's elution.

The concentration of iodide or iodate, released daily, is determined by measurement using an iodine-specific electrode:

Two millilitres of a solution (K_2SO_4 + ascorbic acid) are added to one millilitre of sample from the container - this solution acts as an ion buffer and as a reducing solution in the case where iodates are being measured - together with one millilitre of distilled water. The electrode is immersed in this solution and the electro-chemical potential of the solution is read off. A calibration curve established beforehand using iodide solutions containing 5 x 10^{-5} M/l (M : mole) to 5 x 10^{-2} M/l enables the iodide or iodate concentration (C) to be calculated in mg/l of the solution.

The characteristics of the immersed cylinder are:

Diameter = 10 mm
Height = 20 mm
Surface area = 8.3 cm^2
Volume = 1.72 cm^3
S/V = 4.80 cm^{-1}
Total mass = 2.04 g
Initial quantity of I (Qo) = 0.242 g

The results of the elution kinetics are collated in the following table (Table 1).

Time (days)	Cumulative Q (gram) ACTIVE ION	100 x Q/Qo %
0.25	0.003	1.32
0.92	0.007	2.62
1.92	0.009	3.11
2.25	0.010	3.28
5.00	0.011	3.75
12.00	0.014	4.84
22.00	0.018	5.97
36.00	0.027	9.06
50.00	0.036	12.04

Table 1

Cumulative Q corresponds to the quantity of I equivalent (active ion) eluted at time t.

Knowing that 80% of the active ion incorporated is eluted in accordance with zero-order kinetics with time, the theoretical elution time of the experiment can be calculated using the following expression.

$$\boxed{Te = \frac{0.8 \times Qo}{\text{Daily flow}}} \quad \text{(days)}$$

In the case of Example 1, the theoretical elution time is 333 days.

Example 2.

The procedure is exactly as in Example 1, except that NaI is replaced with 25 parts of KIO_3 with a particle size of between 100 and 200 µm.

A cylinder whose characteristics are as follows is immersed in 600 ml of distilled water, thermostated at 20°C:

Diameter = 10 mm

Height = 20 mm

Surface area = 8.3 cm^2

Volume = 1.72 cm^3

S/V = 4.80 cm^{-1}

Total mass = 2.04 g

Initial quantity of I (Qo) = 0.169 g

The experimental protocol for measuring the elution kinetics is identical with that in Example 1. The results are collated in Table 2 below.

Table 2

Time (days)	Cumulative Q (gram) ACTIVE ION	100 x Q/Qo %
0.92	0.004	2.50
1.92	0.005	3.07
2.25	0.005	3.16
5.00	0.006	3.90
12.00	0.008	4.80
22.00	0.010	6.20
36.00	0.014	8.78
50.00	0.019	11.32

The theoretical elution time for this example is 353 days.

The claims defining the invention are as follows:

1. A diorganopolysiloxane composition which is capable of being cured to a silicone elastomer by a polycondensation reaction, and which comprises:

(A) : at least one diorganopolysiloxane oil carrying at each end of the chain at least two condensable or hydrolysable groups, or a single hydroxyl group,

(B) : from 5 to 130 parts by weight per 100 parts by weight of (A) of an organic and/or inorganic iodine compound, in liquid or solid form at ambient temperature, soluble in water, nontoxic and not inhibiting the cure of the composition to an elastomer,

(C) : a catalyst of polycondensation of the oil, and, when (A) is an oil with hydroxyl end groups,

(D) : a silane containing at least three condensable or hydrolysable groups.

2. A composition according to claim 1, in which the iodine compound (B) is an iodide or iodate of general formulae:

$(M^{a+})(I^{-})a$

and $(M^{a+})(IO_3^{-})a$

in which a is an integer greater than or equal to 1 and M is a cation of an alkali metal, an alkaline-earth metal or a transition metal or is an ammonium cation $(NZ_4)^+$ in which the radicals Z, which may be identical or different, each denote a linear or branched C_1-C_{20} alkyl radical or a hydrogen atom.

3. A composition according to claim 1, in which the iodine compound (B) is:

NaI, $NaIO_3$,
KI, KIO_3,
MgI_2, $MgI_2.8H_2O$,
$Mg(IO_3)_2.4H_2O$,
NH_4I
$FeI_2.4H_2O$, or
MnI_2

4. A composition according to claim 1, in which the iodine compound (B) is calcium iodobehenate.

5. A composition according to claim 1 in which the iodine compound (B) is iodinated polyvinylpyrrolidine.

6. A composition according to any one of the preceding claims, in which the diorganopolysiloxane (A) corresponds to the general formula (1):

$$Y_nSi_{3-n}O(SiR_2O)_xSiR_{3-n}Y_n \qquad (1)$$

in which:

each R, which may be identical or different, is a monovalent hydrocarbon radical, each Y which may be identical or different is a hydrolysable or condensable group, or a hydroxyl group, n is 1, 2 or 3 with n = 1 when Y is a hydroxyl, and x is an integer greater than 1.

7. A composition according to claim 6 in which x is greater than 10.

8. Composition according to claim 6 or 7, in which each R is a C_1-C_8 alkyl, vinyl, phenyl or 3,3,3-trifluoropropyl radical, at least 60% of the radicals R being methyl radicals.

9. A composition according to claim 6, 7 or 8, in which Y is an amino, acylamino, aminoxy, ketiminoxy, iminoxy, enoxy, alkoxy, alkoxyalkyleneoxy, acyloxy or phosphate group.

10. A composition according to any one of the preceding claims which contains a silane (D) which corresponds to the formula:

$$R_{4-a}SiY'a \qquad (2)$$

in which R is a monovalent hydrocarbon radical, each Y' which may be identical or different is a hydrolysable or condensable group and a is 3 or 4.

11. A composition according to any one of the preceding claims, in single-component form.

12. Composition according to any one of claims 1 to 10 in two-component form.

13. Composition according to claim 12, comprising:

(A) : 100 parts by weight of an alpha,omega-dihydroxyorganopolysiloxane oil with a viscosity of 50 to 300,000 mPa s in which each organic radical is a methyl, ethyl, vinyl, phenyl or 3,3,3-trifluoropropyl radical, at least 60% being methyl radicals, up to 20% being phenyl radicals, and not more than 2% being vinyl radicals,

(B) : 10 to 130 parts by weight of an iodine compound,

(C) : 0.01 to 1 part by weight (calculated as the weight of tin metal) of a catalytic tin compound,

(D) : 0.5 to 15 parts by weight of a polyalkoxysilane or a polyalkoxysiloxane, and

(E) : 0 to 100 parts by weight of siliceous inorganic filler.

14. A composition according to claim 13 in which (E) is present in an amount 5 to 50 parts by weight.

15. A composition according to claim 1 substantially as described in Example 1.

16. A composition according to any one of the preceding claims, cured to an elastomer.

17. A water treatment process in which an elastomer as defined in claim 16 is immersed in water to release a continuous and controlled quantity of iodine into the water.

~~18. A composition according to claim 1 in all its new and useful aspects~~.

DATED THIS 24th DAY OF FEBRUARY 1988
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By its Patent Attorneys
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