MICROCOPY RESOLUTION TEST CHART
NATIONAL BUREAU OF STANDARDS
STANDARD REFERENCE MATERIAL 1010a
(ANSI and ISO TEST CHART No. 2)
COMMONWEALTH of AUSTRALIA
PATENTS ACT 1952
APPLICATION FOR A STANDARD PATENT

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

We hereby apply for the grant of a Standard Patent for an invention entitled:
"COMPOSITIONS BASED ON DIORGANOPOLYSILOXANE RESIN CONTAINING IODINE FOR WATER TREATMENT"

which is described in the accompanying specification.

Details of basic application(s):

<table>
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<tr>
<th>Number</th>
<th>Convention Country</th>
<th>Date</th>
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<tr>
<td>8702882</td>
<td>FRANCE</td>
<td>26th February 1987</td>
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</table>

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

(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

In support of the Application made for a patent entitled: "COMPOSITION BASED ON DIOXIRONDIOXYLUXANE RESIN CONTAINING IODINE FOR WATER TREATMENT"

I, Jean-Louis Seguret,
OP: RHONE-POULENC CHIMIE, a French body corporate, of: 25, Quai Paul Doumer, 92408 COURBEVOIE, France.

do solemnly and sincerely declare as follows:

I am the applicant for the patent or I am authorized by RHONE-POULENC CHIMIE the applicant to make this declaration on its behalf.

2. We are the actual inventors of the invention.

(a) Guy Cyrienne, Alain Fish, Johnny Baggiage,
Hugues Porte, Thierry Prazuck and Gilleslane Torres, all French citizens of: 7, rue d'Anjou, 92240 L'HAY LES ROSES, France; 22, rue de l'Yvette, 75016 PARIS, France; 72, rue du Port Saint-Irene, 69005 LYON, France 6, chemin de Crepieux, 69300 CALUIRE, France: 53 avenue Mathurin Moureau, 75019 PARIS, France and 104, rue Ney, 69006 LYON, France, respectively.

I, the actual inventor, am entitled to make the application as follows:

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

3. The basic application as defined by Section 141 of the Act was made in FRANCE: NO. 87/02 882 on the 26th February, 1987

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

Declared at Saint-Paul this 12 day of January 1987

[Signature]
Jean-Louis Seguret
Inventeur-Savete
Claim

1. Silicone composition comprising (A) a diorganopolysiloxane resin, (B) a reinforcing filler (B₁), and/or an organic peroxide (B₂), and (C) at least one organic and/or inorganic iodine compound in a solid or liquid form at ambient temperature, soluble in water and nontoxic, in an amount from 5 to 150 parts of said iodine compound (C) per 100 parts of resin (A).

14. An elastomer produced by curing a composition according to any one of claims 1 to 13 by heating.

15. A process for iodizing water which comprises treating said water with an uncured composition as defined in any one of claims 1 to 13 so as to release a continuous and controlled quantity of iodine into said water.

16. A process for iodizing water which comprises treating said water with a cured composition as defined in claim 14 so as to release into said water a continuous and controlled quantity of iodine.
COMPLETE SPECIFICATION FOR THE INVENTION ENTITLED:

"COMPOSITION BASED ON DIORGANOPOLYSILOXANE RESIN CONTAINING IODINE FOR WATER TREATMENT"

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 compositions containing iodine, useful for iodizing 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 campaigns 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 ingestion, especially for ruminants (French Patent FR-A-2,560,768).

Lastly, US Patent US-A-4,384,960 describes the placing of iodine (I₂) tablets in a plastic bottle into which water enters through a porous polymer 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. This suggested solution is however not technically feasible because, on the one hand, I₂ is a well-known inhibitor of the catalyst 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)) and, on the other hand, I₂ sublimes during the crosslinking of silicone elastomers by heat because of its high volatility.

Moreover, in this system, 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 silicone composition containing iodine which is capable of being employed for the continuous treatment of water for domestic use, particularly in water supply and treatment systems in wells and boreholes, and which makes it possible to distribute (release) a controlled and adapted quantity of iodine with a view to ensuring both the collective treatment of the various manifestations of iodine deficiency and prevention of these various manifestations.

The new silicone compositions containing iodine, 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 quantity of iodine in a therapeutically active and effective form and dosage to treat the various diseases caused by iodine deficiency.

The new compositions have no undesirable secondary action which is detrimental to the water to be treated from a chemical or biological standpoint.
The new silicone compositions containing iodine are adapted to the environment in which the water to be treated is found, and are particularly well adapted to wells and/or boreholes, and they can be easily replaced.

The silicone compositions of the present invention comprise:

(A) a diorganopolysiloxane resin,
(B) a reinforcing filler (B₁) and/or an organic peroxide
(C) at least one organic and/or inorganic iodine compound in solid or liquid form at ambient temperature, soluble in water and nontoxic in an amount from 5 to 150 parts of said iodine compound (C) per 100 parts of resin (A).

With the exception of molecular iodine I₂, the inorganic iodine compound employed, by itself or mixed, may be:
- an iodine or iodate of formula:

\[(\text{M}^+\text{I}^-)_a\]

or

\[(\text{M}^+\text{I}_3^-)_a\]

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, or an ammonium cation \((\text{NY}_4)^+\), in which the radicals \(Y\), which may be identical or different, each denote a linear or branched \(\text{C}_1-\text{C}_{20}\) alkyl radical or a hydrogen atom, such as the ammonium ion \(\text{NH}_4^+\).

The cations \(\text{M}^{a+}\) and \(\text{NY}_4^+\) 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 include 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:

\[(\text{C}_{21}\text{H}_{42}\text{ICO}_2)\text{Ca}\]

Iodinated polyvinylpyrrolidone may be mentioned as an organic iodine compound.

For reasons of ease of use, solid iodine compounds
are preferred, and NaI and KI03 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.

From 5 to 150 parts and preferably from 10 to 100 parts of iodine compound (C) are generally employed per 100 parts of resin (A).

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 10-12 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 where goitre is highly endemic, the preexisting proportion 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.

Unless indicated otherwise, the parts and percentages in what follows or what precedes are given by weight.

Surprisingly and unexpectedly, it has been found, in fact, according to the present invention, that it is possible to add into a silicone resin large quantities of iodine compound in a solid or liquid form such as defined above, namely from 5 to 150 parts, preferably from 20 to 100 per 100 parts of diorganopolysiloxane filled resin with a reinforcing filler beforehand and thus to obtain a product which, even in the absence of a crosslinking and/o or antistructuring agent has sufficient 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 principal. 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 according to the invention 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 parallele-
pipeds, 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 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 dilution time which will correspond to the actual time of diffusion of the active ingredient.

In the case of NaI and KI0$_3$, which are the preferred iodine compounds, $g$, $t$ and $R$ may be advantageously chosen within the following ranges:

- $g$ of between 1 and 300 $\mu$m,
- 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.

More precisely, the present invention relates to a silicone composition comprising:

- (A): 100 parts of a diorganopolysiloxane resin having a viscosity greater than 1 million mPa s at 25°C,
- (B): 5 to 130 parts of a reinforcing, preferably siliceous, filler (B₁), chosen from pyrogenic silicas and precipitated silicas, and/or from 0.1 to 6 parts of an organic peroxide (B₂), and
- (C): 5 to 150 parts of an organic and/or inorganic iodine compound, solid at ambient temperature, soluble in water and nontoxic.

More particularly, the diorganopolysiloxane resin (A) has the general formula $R_3 - a(R'0)_{2a}SiO(R_2SiO)_nSi(OR')_{a-R3-a}$, in which the symbols R, which may be identical or different, denote C₁-C₈ hydrocarbon radicals, substituted or otherwise by halogen atoms or cyano radicals, the symbol R' denotes a hydrogen atom or a C₁-C₄ alkyl radical, the symbol a denotes zero or one, and the symbol n denotes a number having a sufficient value to produce a viscosity of at least 1 million mPa s at 25°C, and at least 50% of the...
number of radicals denoted by R are methyl radicals.

0.005 to 0.5 mole % of the units forming part of the constitution of the resin (A) are preferably chosen from those of formulae \((CH_2=CH)(R)SiO\) and/or

\[(CH_2=CH)R_2-a(RO')_aSi0.5\]

The resin (A) with a viscosity of 1 million mPa s at 25°C, preferably of at least 2 million mPa s at 25°C, is made up, along its chain, of \(R_2SiO\) units and it is blocked by an \(R_3-aR(O)_aSi0.5\) unit at each end of its chain; however, the presence of units of different structure mixed with these units, for example of formula \(RSiO1.5\) and \(SiO_2\), is not ruled out in the proportion of not more than 2% based on the total number of the \(R_2SiO\) and \(R_3-a(RO')_aSi0.5\) units.

The symbol R denotes a \(C_1-C_8\) hydrocarbon radical substituted or otherwise by halogen atoms or cyano radicals; more specifically, it includes:

- \(C_1-C_5\) alkyl radicals, substituted or otherwise by halogen atoms or cyano radicals, such as methyl, ethyl, propyl, isopropyl, butyl, isobutyl, pentyl, 3,3,3-trifluoropropyl, \(\beta\)-cyanoethyl and \(\gamma\)-cyanopropyl radicals,
- \(C_2-C_4\) alkenyl radicals such as vinyl, allyl and 2-butenyl radicals, and
- \(C_6-C_8\) monocyclic aryl radicals, substituted or otherwise by halogen atoms, such as phenyl, chlorophenyl, tolyl and trifluoromethylphenyl radicals.

The \(C_1-C_4\) alkyl radicals denoted by the symbol
R' relate more specifically to methyl, ethyl, propyl, isopropyl, butyl and secondary butyl radicals.

At least 50% on a numerical basis, preferably at least 70%, of the radicals denoted by R are methyl radicals.

Furthermore, vinyl radicals are also preferably present in a suitable quantity in the resin (A); they result in units of formula \( CH_2=CH(R)SiO \) and \( CH_2=CH(R_{2-a})(R'0)_aSiO_{0.5} \), whose number represents 0.005 to 0.5 mole %, preferably 0.01 to 0.45 mole %, of the total of the units of general formulae \( R_2SiO \) and \( R_{3-a}(R'0)_aSiO_{0.5} \), forming part of the constitution of the resin (A).

By way of concrete examples of units forming the resins (A) there may be mentioned those of formulae:

\[
\begin{align*}
(CH_3)_2SiO, \\
CH_3(CH_2=CH)SiO, \\
CH_3(C_6H_5)SiO, \\
(C_6H_5)2SiO, \\
CH_3(C_2H_5)SiO, \\
CH_3CH_2-CH_2(CH_3)SiO, \\
CH_3(n-C_3H_7)SiO, \\
(CH_3)3SiO_{0.5}, \\
(CH_3)_2CH=CHSiO_{0.5}, \\
CH_3(C_6H_5)2SiO_{0.5}, \\
CH_3(C_6H_5)(CH_2=CH)SiO_{0.5}, \\
HO(CH_3)_2SiO_{0.5},
\end{align*}
\]
The resins (A) are marketed by the manufacturers of silicones; furthermore, they may be readily manufactured by using methods which are abundantly described in the chemical literature.

In the majority of cases, use is made of methylvinyldimethylpolysiloxane resins containing \( (\text{CH}_3)_2\text{SiO} \) and \( \text{CH}_2=\text{CH}(\text{CH}_3)\text{SiO} \) units along their chain and, at the end of their chain, units chosen from those of formulae:

\[
\begin{align*}
\text{CH}_3\text{O}(\text{CH}_3)_2\text{SiO}_{0.5}, \\
\text{C}_2\text{H}_5\text{O}(\text{CH}_3)_2\text{SiO}_{0.5}, \\
n-\text{C}_3\text{H}_7\text{O}(\text{CH}_3)_2\text{SiO}_{0.5}, \\
\text{HO.}(\text{CH}_2=\text{CH})(\text{CH}_3)\text{SiO}_{0.5},
\end{align*}
\]

or dimethylpolysiloxane resins blocked at each end of their chain by one of the preceding units containing a vinyl radical.

They generally have a viscosity of at least 2 million mPa s at 25°C.

The fillers (B₁) which are preferably reinforcing silicas are employed in a proportion of 5 to 130 parts of diorganopolysiloxane resins (A). They are chosen from combustion silicas and precipitated silicas. They have a specific surface area, measured according to the BET methods, of at least 50 m²/g, preferably greater than 70 m²/g, a mean dimension of the primary particles of less
than 0.1 μm (micrometre) and an apparent density of less than 200 g/litre.

These silicas may be incorporated as such or after they have been treated with the organosilicon compounds 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, methylvinylidichlorosilane and dimethylvinylchlorosilane, and alkoxy silanes such as dimethyldimethoxy- silane, dimethylvinylethoxysilane and trimethylmethoxy- silane. In the course of this treatment, the silicas may increase in their initial weight up to a proportion of 20%, preferably approximately 18%.

The compositions according to the invention may be kneaded cold as such and may be extruded, for example, in the form of a cylinder with a diameter of between 0.5 and 9 cm. The cylinders of silicone composition which are obtained may be cut to the desired length in the case of their utilization in boreholes so that the cylinder may contain a sufficient quantity of iodine equivalent for a release during one year.

It has surprisingly been found that these un- crosslinked silicone compositions have physical characteristics which are sufficient for the intended applications and release iodine in a continuous and controlled
manner. An organic peroxide \((B_2)\) may be employed within the scope of the present invention, in addition to \((B_1)\) or instead of \((B_1)\) or at the same time as \((B_1)\). The elastomeric composition must then be cross-linked when hot.

The organic peroxides \((B_2)\) are employed in a proportion from 0.1 to 6 parts, preferably 0.2 to 5 parts, per 100 parts of the resins \((A)\). They are well known to the specialists and include more especially benzoyl peroxide, 2,4-dichlorobenzoyl peroxide, dicumyl peroxide, 2,5-bis(t-butylperoxy)-2,5-dimethylhexane, t-butyl perbenzoate, t-butylperoxy isopropyl carbonate, di-t-butyl peroxide and 1,1-bis(t-butylperoxy)-3,3,5-trimethylcyclohexane.

These various peroxides decompose at temperatures and at rates which are sometimes different. They are chosen as a function of the required cure conditions.

The silicone compositions according to the invention may additionally contain, per 100 parts of resin \((A)\), from 0.1 to 6 parts of an antistructuring agent \((D)\) which is an organic fluorine polymer in the form of a pulverulent solid.

The fluorine polymers \((D)\) are employed in a proportion of 0.1 to 6 parts, preferably 0.15 to 5 parts, per 100 parts of the diorganopolysiloxane resins \((A)\). These compounds are well known to the specialists: they are prepared by polymerization or copolymerization of
monomers chosen, for example, from the group of tetrafluorethylene, chlorotrifluoroethylene, vinylidene fluoride and hexafluoropropene. They are therefore polymers or copolymers consisting of units derived from the above-mentioned monomers; polytetrafluoroethylenes, binary copolymers of the polytetrafluoroethylene/beta-fluoropropene or of the vinylidene fluoride/hexafluoropropene type, and ternary copolymers of the vinylidene fluoride/hexafluoropropene/tetrafluoroethylene type may thus be employed.

These compounds may be introduced into the compositions of the invention in the form of powders with a mean particle diameter of less than 100 micrometres, for example with a diameter ranging from 25 to 65 micrometres.

When the crosslinking agents (B₂) are employed, preferably up to 90% by weight of the reinforcing silicas (C) may be replaced with semireinforcing or extender fillers whose particle diameter is greater than 0.1 μm, such as ground quartz, calcined clays and diatomaceous earths.

The silicone compositions may additionally comprise from 1 to 10 parts of dimethylpolysiloxane oils (E) with silanol ends with a viscosity of between 10 and 5,000 mPa s, preferably from 30 to 1,000 mPa s, at 25°C, per 100 parts of resin (A). Their use is especially recommended when the quantities of reinforcing fillers (B₁) are high.

The preparation of the compositions according to
the invention is carried out with the aid of known mechanical means, for example dough mixers, roll mills and screw mixers.

The various constituents are incorporated in these pieces of equipment in an order which may be immaterial. It is recommended, nevertheless, to charge the resin (A) and then, in order, the siliceous fillers (B₁) and the iodine compound (C), the additive (E) if desired and, lastly, the compound (D) and (B₂).

The compositions obtained are stable in storage; furthermore, they are easily moulded and extruded, and this permits very varied shapes to be produced. Those containing peroxide (B₂) are crosslinked by being heated. The heating time obviously varies with the temperature, the pressure and the nature of the crosslinkers. It is generally of the order of a few minutes at about 150-250°C and of a few seconds at about 250-350°C.

The elastomers formed in this manner may be subsequently post-heated if desired, particularly those obtained by moulding for a period of at least one hour at a temperature of between 190 and 270°C with the objective of completing their crosslinking.

Nevertheless, as soon as their first crosslinking stage is finished, that is to say before any post-heating stage, these elastomers have sufficient physical characteristics for the intended application.

The silicone compositions, optionally crosslinked,
are advantageously in the form of modules (elements) of various shapes. The quantity of iodine and the release period are determined for a given module.

Thus, an appropriate number of modules may be immersed in the water to be treated, which corresponds 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.

It has surprisingly been found that these silicone compositions, optionally crosslinked, have sufficient physical characteristics for the intended applications.

The following Examples illustrate the invention.

**Example 1**

**Preparation of the composition**

Composition: the following ingredients are intimately mixed with the aid of a kneader.

100 parts of a dimethylmethylnvinylpolysiloxane resin (A) blocked by a trimethylsiloxy unit at each of its two ends and containing 99.8 mol % of dimethylsiloxyl units and 0.2 mol % of vinylmethyilsiloxyl units in its chain and with a viscosity of 10 million mPa.s at 25°C,

43.5 parts of filler (B) which is a D4 (octamethylcyclotetrasiloxane)-treated combustion silica with a BET specific surface area of 300 m²/g,

1 part of a linear dimethylpolysiloxane blocked
with dimethylhydroxysiloxane groups at both of its ends, with a viscosity of 50 mPa s,

0.2 part of octamethyltetracyclo siloxane,

37.2 parts of NaI of mean particle size equal to 5 µm (C).

The kneading is stopped 30 minutes after the end of the addition of silica. The homogeneous composition which has just been prepared is removed from the kneader and is called the master mixture (MM).

The MM is transferred to a roll mill in order to incorporate, per 100 parts of MM:

0.5 part of 2,5-dimethyl-2,5-di(tert-butylperoxy)-hexane.

The catalysed composition separates readily from the mill rolls. It is then extruded into a continuous sausage 26 mm in diameter which is then cured by being passed through a 6-m oven heated to 350°C at a speed of 1 m per minute. A uniform rod is obtained, which is then reheated for 4 hours at 150°C.

**Experimental protocol for measuring the elution kinetics**

The elastomeric composition containing NaI is cut to the desired length (35.4 mm), in accordance with the surface/volume ratio (2.08 cm⁻¹) which it is desired to obtain and is immersed in a container of 500 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 iodide-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 electrochemical potential of the solution is read off. A calibration curve established beforehand using iodide solutions containing $5 \times 10^{-5}$ M/l (M: mole) to $5 \times 10^{-2}$ 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: 26.3 mm
- Height: 35.4 mm
- Surface area: 40.1 cm$^2$
- Volume: 19.23 cm$^3$
- $S/V$: 2.08 cm$^{-1}$
- Total mass: 19.89 g
- Initial quantity of I($Q_o$): 3.36 g

The results of the elution kinetics are collated...
in Table 1, in which Q corresponds to the quantity of I equivalent (which we call active ion) eluted at time t.

Table 1

<table>
<thead>
<tr>
<th>TIME t (DAYS)</th>
<th>Cumulative Q (gram) active ion</th>
<th>100*Q/Q0 (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.19</td>
<td>0.189</td>
<td>5.60</td>
</tr>
<tr>
<td>0.98</td>
<td>0.297</td>
<td>8.81</td>
</tr>
<tr>
<td>2.01</td>
<td>0.341</td>
<td>10.13</td>
</tr>
<tr>
<td>6.92</td>
<td>0.355</td>
<td>10.53</td>
</tr>
<tr>
<td>11.02</td>
<td>0.356</td>
<td>10.62</td>
</tr>
<tr>
<td>15.92</td>
<td>0.428</td>
<td>12.70</td>
</tr>
<tr>
<td>17.92</td>
<td>0.440</td>
<td>13.05</td>
</tr>
<tr>
<td>24.97</td>
<td>0.431</td>
<td>12.79</td>
</tr>
<tr>
<td>35.20</td>
<td>0.432</td>
<td>12.83</td>
</tr>
<tr>
<td>45.91</td>
<td>0.535</td>
<td>15.89</td>
</tr>
<tr>
<td>52.23</td>
<td>0.468</td>
<td>13.89</td>
</tr>
<tr>
<td>60.19</td>
<td>0.522</td>
<td>15.50</td>
</tr>
<tr>
<td>73.21</td>
<td>0.622</td>
<td>18.45</td>
</tr>
<tr>
<td>77.12</td>
<td>0.622</td>
<td>18.47</td>
</tr>
<tr>
<td>91.12</td>
<td>0.602</td>
<td>17.86</td>
</tr>
<tr>
<td>115.92</td>
<td>0.712</td>
<td>21.13</td>
</tr>
<tr>
<td>150.16</td>
<td>0.726</td>
<td>21.56</td>
</tr>
</tbody>
</table>
Knowing that 80% of the active ion incorporated is eluted in accordance with zero-order kinetics with time, we can calculate the theoretical elution time (Te) for each example according to:

\[
    \text{Te} = \frac{0.8 \times Q_0}{\text{daily flow}} \quad \text{(days)}
\]

In the case of this Example, Te is 640 days.

**Example 2**

The composition employed is the same as in Example 1, except that 37.2 parts of KI03 are incorporated, with a particle size of between 100 and 200 μm.

The kneading is stopped 30 minutes after the end of the addition of silica. The homogeneous composition which has just been prepared is removed from the kneader and is called the master mixture (MM).

The MM is transferred to a roll mill in order to incorporate, per 100 parts of MM:

0.5 part of 2,5-dimethyl-2,5-di(tert-butylperoxy)-hexane.
The catalysed composition separates readily from the mill rolls. It is then extruded into a continuous sausage 23 mm in diameter which is then cured by being passed through a 6-m oven heated to 350°C at a speed of 1 m per minute. A uniform rod is obtained, which is then reheated for 4 hours at 150°C.

A cylinder is then cut off, whose characteristics are as follows:

- Diameter: 23.0 mm
- Height: 50.0 mm
- Surface area: 44.4 cm²
- Volume: 20.76 cm³
- S/V: 2.14 cm⁻¹
- Total mass: 25.37 g
- Initial quantity of I(Q0): 3.01 g

The results of the elution kinetics are collated in Table 2. The theoretical elution time of this Example is 1170 days.
### TABLE 2

<table>
<thead>
<tr>
<th>TIME (DAY) (t)</th>
<th>Cumulative Q (grams)</th>
<th>$100 \times \frac{Q}{Q_0}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.12</td>
<td>0.009</td>
<td>0.31</td>
</tr>
<tr>
<td>0.29</td>
<td>0.010</td>
<td>0.34</td>
</tr>
<tr>
<td>1.00</td>
<td>0.018</td>
<td>0.58</td>
</tr>
<tr>
<td>2.00</td>
<td>0.022</td>
<td>0.71</td>
</tr>
<tr>
<td>6.00</td>
<td>0.035</td>
<td>1.15</td>
</tr>
<tr>
<td>8.00</td>
<td>0.045</td>
<td>1.45</td>
</tr>
<tr>
<td>12.00</td>
<td>0.051</td>
<td>1.66</td>
</tr>
<tr>
<td>15.00</td>
<td>0.053</td>
<td>1.74</td>
</tr>
<tr>
<td>21.00</td>
<td>0.065</td>
<td>2.12</td>
</tr>
<tr>
<td>26.00</td>
<td>0.071</td>
<td>2.32</td>
</tr>
<tr>
<td>33.00</td>
<td>0.082</td>
<td>2.67</td>
</tr>
<tr>
<td>40.00</td>
<td>0.091</td>
<td>2.98</td>
</tr>
<tr>
<td>49.00</td>
<td>0.104</td>
<td>3.41</td>
</tr>
<tr>
<td>61.00</td>
<td>0.116</td>
<td>3.78</td>
</tr>
<tr>
<td>79.00</td>
<td>0.141</td>
<td>4.60</td>
</tr>
<tr>
<td>96.00</td>
<td>0.161</td>
<td>5.24</td>
</tr>
<tr>
<td>117.00</td>
<td>0.182</td>
<td>5.92</td>
</tr>
</tbody>
</table>
The claims defining the invention are as follows:

1. Silicone composition comprising (A) a diorganopolysiloxane resin, (B) a reinforcing filler (B₁) and/or an organic peroxide (B₂), and (C) at least one organic and/or inorganic iodine compound in a solid or liquid form at ambient temperature, soluble in water and nontoxic, in an amount from 5 to 150 parts of said iodine compound (C) per 100 parts of resin (A).

2. Silicone composition according to claim 1, in which the compound (B) is a siliceous reinforcing filler.

3. Silicone composition according to claim 1 or 2, in which iodine compound (C) is an iodide or iodate of formula:

$$(M^{n+})(I^-)_a$$

or

$$(M^{n+})(IO_3^-)_a$$

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 an ammonium cation ($NY_4$)$^+$ in which the radicals Y, which may be identical or different, each denote a linear or branched C₁-C₂₀ alkyl radical or a hydrogen atom.
4. Composition according to claim 3, in which the iodine compound (C) is:
   NaI, NaIO₃,
   KI, KIO₃,
   5 MgI₂, MgI₂·8H₂O,
   Mg(IO₃)₂·4H₂O,
   NH₄I,
   FeI₂·4H₂O, or
   MnI₂

5. Composition according to claim 1 or 2, in which the iodine compound (C) is calcium iodobehenate.

6. Composition according to claim 1 or 2, in which the iodine compound (C) is iodinated polyvinylpyrrolidone.

7. Composition according to any one of the preceding claims, which comprises:
   - (A): 100 parts by weight of a diorganopolysiloxane resin having a viscosity of at least 1 million mPa s at 25°C,
   - (B): 5 to 130 parts by weight of a reinforcing siliceous filler (B₁) which is a pyrogenic silica or a precipitated silica, and
   - (C): 5 to 150 parts by weight of an organic and/or inorganic iodine compound, which is solid at ambient 25 temperature, soluble in water and nontoxic.
8. Composition according to any one of the preceding claims, in which the resin (A) has the general formula \( R_{3-a} (R'0) \cdot SiO (R_2 SiO) \cdot Si(OR') \cdot R_{3-a} \), in which the symbols \( R \), which may be identical or different, each denote a \( C_1 - C_8 \) hydrocarbon radical, which is unsubstituted or substituted by halogen or cyano, the symbol \( R' \) denotes a hydrogen atom or a \( C_1 - C_4 \) alkyl radical, the symbol \( a \) denotes zero or one, and the symbol \( n \) denotes a number having a sufficient value to produce a viscosity of at least 1 million mPa s at 25°C, and at least 50% of the radicals denoted by \( R \) are methyl radicals.

9. Composition according to claim 8, in which 0.005 to 0.5 mol % of the units forming part of the resin (A) have the formula \((CH_2 = CH)(R)SiO\) or \((CH_2 = CH)R_{2-a} (RO')_a SiO_\cdot 5\).

10. Composition according to any one of the preceding claims, which additionally comprises from 0.1 to 6 parts of an antistructuring agent (D) which is an organic fluorine polymer in pulverulent solid form.

11. Composition according to any one of the preceding claims which comprises both the reinforcing filler (B_1), and from 0.1 to 6 parts of the organic peroxide (B_2).
12. Composition according to claim 11, in which up to 90% by weight of the reinforcing silicone filler (B₁) is replaced by semireinforcing or extending fillers.

13. A composition according to claim 1 substantially as described in Example 1 or 2.

14. An elastomer produced by curing a composition according to any one of claims 1 to 13 by heating.

15. A process for iodizing water which comprises treating said water with an uncured composition as defined in any one of claims 1 to 13 so as to release a continuous and controlled quantity of iodine into said water.

16. A process for iodizing water which comprises treating said water with a cured composition as defined in claim 14 so as to release into said water a continuous and controlled quantity of iodine.

17. A process according to claim 16 substantially as described in Example 1 or 2.

18. The hereinbefore described invention in all its new and useful aspects.

DATED THIS 24th DAY OF FEBRUARY 1988
RHONE-POULENC CHIMIE
By its Patent Attorneys
DAVIES & COLLISON
END