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Organosilicon Liquid Rubbers and Materials Based on them

O N Dolgov, M G Voronkov, M P Grinblat

Translated from the Russian by

R J Moseley

International Polymer Science and Technology Monograph, No. 1

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КРЕМНИЙОРГАНИЧЕСКИЕ ЖИДКИЕ КАУЧУКИ И МАТЕРИАЛЫ НА ИХ ОСНОВЕ

O.N. Dolgov, M.G. Voronkov, M.P. Grinblat

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This series of monographs represents a further stage of development in the joint collaboration between the British Library Lending Division, and the Rubber and Plastics Research Association of Great Britain towards the provision in the English language of information on polymers published initially overseas. This collaboration began with the cover-to-cover translation of two Russian periodicals and is currently exemplified by 'International Polymer Science and Technology', a monthly journal containing around 40 translations selected from the original two periodicals plus others in Russian, Eastern European languages and Japanese. Further details of this journal are given overleaf.

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International Polymer Science and Technology

This monthly journal, published by RAPRA and sponsored by the British Library, represents a translation service which enables subscribers to scan sets of abstracts from current issues of a wide range of European and Japanese rubber and plastics journals and, on this basis, to recommend articles for translation. The translations are published, together with the abstracts, in the journal, and the subscribers requesting a given translation can receive an advance copy of that translation if desired.

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This service, which is now entering Volume 4, is the successor to the RAPRA cover-to-cover translation journals 'Soviet Plastics' and 'Soviet Rubber Technology'. The translation team comprises Mr. E.A. Inglis, Mr. R.J. Moseley and Mr. P.G. Williams, with Dr. J.R. Scott as the Consultant Editor.

International Polymer Science and Technology thus provides facilities, at an economical subscription, for translations from six major languages of importance in the polymer field.

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*Coverage of Journals 1977

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The British Library LENDING DIVISION
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The British Library. Lending Division (BLLD) has an extensive programme of commissioning and publishing translations of research materials, which covers the translation of whole journals as well as books and individual articles. The two main aims are clearly related to the main function of the library: to improve access of researchers to significant literature in foreign languages, especially Russian and Japanese; and to increase the library's stock of literature in English to meet the needs of users who cannot read the original. The whole programme is the responsibility of the Translating Section of the BLLD (to which any enquiries should be addressed).

TRANSLATED JOURNALS

The BLLD sponsors the publication of several journals (currently 12) consisting entirely of translations. The translating, editing, printing and distribution of each journal are carried out on the library's behalf by learned societies, research associations and commercial publishers. The majority are cover-to-cover translations of single Russian journals, some being selective in that ephemeral or non-scientific articles are omitted and two contain articles selected from more than one journal. The first of these, STEEL IN THE USSR, is based on articles appearing in two Russian metallurgical journals, and the second, INTERNATIONAL POLYMER SCIENCE AND TECHNOLOGY (IPST), is based on a number of Russian, East European and Japanese polymer science journals.

TRANSLATED BOOKS

The BLLD is also prepared to organise and publish the translation of books, the requester being expected to edit the translation and make a contribution towards the cost of having it produced. Currently, about five book translations are produced in this way every year. They are announced in BRITISH NATIONAL BIBLIOGRAPHY and are available for purchase from the BLLD. The library has, to date, published translations of over 130 books in a variety of fields. Some have been produced in conjunction with commercial publishers; others have been produced by the BLLD on the advice of an individual who is an expert in the field. No subject restriction is applied to the BLLD service, but in practice most requests are in the fields of science and technology.

TRANSLATED ARTICLES

Since the early 1960s the National Lending Library for Science and Technology (NLLST), and later the BLLD, has provided an AD HOC translating service for articles as well as books. The service was initially concerned with science and technology but now covers all subject fields. The scheme was originally restricted to the translation of articles and books from Russian; this was extended in 1968 to other Cyrillic languages and to Japanese in 1969, to other Slavonic languages in 1974, to German in 1974, and in 1976 to all languages. The conditions under which translations can be supplied under this service have remained largely unchanged:

(i) If possible an English abstract/summary should have been checked to ensure that the translation is really needed. Where such a summary has not been consulted, the library will endeavour to provide one.
(ii) The article must not be from a journal scheduled for translation from cover-to-cover.
(iii) The translation must be edited by the requester.
(iv) The translation must be for private use and not for publication.

Charges were introduced at the end of 1974, the aim being to recover the expenditure on translators' fees but not overheads, staff costs, accommodation, or materials. The person requesting the translation was charged an amount calculated to produce one-third of the fees, the remaining two-thirds being recouped from subsequent sales, on the basis that there are on average three subsequent requests for each translation. Predictably, there was a reduction in demand for the service as a result of the imposition of charges, but recently demand has begun to increase, and around 700 requests are expected in 1977.

In 1976, Translating Section produced the catalogue TRANSLATED BOOKS AVAILABLE FROM THE BLLD, which lists the bibliographic details of each translated book produced by the NLLST/BLLD, and gives a brief description of the contents. This is available from BLLD free of charge. At present, a similar catalogue is being prepared of the 11,000 + AD HOC translations which have been made, but this is being produced in subject sections. The section on macromolecular materials will shortly be completed, and will be available free from the Translating Section. Other relevant sections, e.g. chemical engineering, will be appearing in due course.

In addition to cooperating in the publication of IPST, the BLLD and RAPRA are currently cooperating in the production of translations of significant Russian books. The first of this series is now available, price £15.00, from either organisation. This is the first of a series, and readers are invited to submit suggestions for future titles which appear to be of significance in the broad field of rubber and plastics technology.

AUTHOR'S FOREWORD

The development of modern technology promotes the creation of new materials with a specific combination of useful properties. These materials include organosilicon elastomers, which have relatively good resistance to low and high temperatures, good elasticity, good dielectric properties, resistance to weathering, moisture and ozone, and biological inertness. Along with heat-curing organosilicon rubbers based on high-molecular silicone rubbers there is increasing use of cold-curing compositions based on low-molecular polyorganylsiloxanes. These compositions are now being used with success in space and rocket technology, aviation, radio and electronics, building, consumer goods, medicine and so forth.

The production and use of silicone rubbers are rising continuously. This is brought about both by expansion of their uses and by the achievements in their synthesis. Not counting the Soviet Union, there were used in 1970 30,000 tonnes of heat-curing silicone rubbers and 13,000 tonnes of cold-curing rubbers. The rate of increase in the use of RTV rubbers is markedly higher than for heat-curing vulcanisation (10—15 and 6—9% respectively), this being explained mainly by their simplicity and handiness of employment.

In recent years the cost of all types of organosilicon products, including cold-curing compositions, has been falling steadily. For instance, in 1970 the cost of organosilicon rubbers fell on an average by 25—50%, and outside the Soviet Union is 4.5—5.5 dollars per kg. In the sale of large consignments the cost of single-component silicone compositions fell by 25% (from 9.9 to 7.4 dollars for 1 kg), that of two-component compositions by 30% (from 12.5 to 8.9 dollars per 1 kg).

In spite of a vast number of publications (mostly patents) describing methods of production and directions of use of RTV silicone compositions, nowhere in the world has there been published a single review article or monograph dealing specifically with this question.

In this book we describe in detail the methods of production and the properties of cold-curing organosilicon compositions, their fields of use and the conditions of service. The discussion of these questions is preceded by a short description of the methods of synthesis of low-molecular organosilicon elastomers, which are the basis of cold-curing silicone compositions.

The authors express their deep indebtness to Dokt. Khim. Nauk F.A. Galil-Ogly, Kand. Khim. Nauk Z.N. Nudel'man and Kand. Khim. Nauk V.P. Mileshkevich, who studied the monograph in m/s form and made a number of valuable critical comments which were taken in account in the subsequent work.

TRANSLATOR'S FOREWORD

This book is the first in a series of monographs to be published as part of the established 'International Polymer Science and Technology' journal and translations service. The policy of selection of books for translation in this series is that they add significantly to the store of information published in English on polymer science and technology. Consequently this first book has been chosen for translation because it remains the only exhaustive survey published on liquid, cold-vulcanising, organosilicon compositions.

The successful culmination of any project requires the help of a number of people. At RAPRA, technical assistance has been afforded by Mr. V.J. Beddoes, Dr. S.H. Morrell and Dr. J.R. Scott and the lay-out and printing has been carried out by Mrs. R.A. Amos and her department. The major translating activities at RAPRA have been encouraged by the staff at the British Library, Lending Division, principally Mr. A.G. Myatt, Mr. G.R. Parker and Miss B. Smith. The translator gratefully acknowledges the help given to him by all of those mentioned.

Finally, acknowledgement must be paid to the Copyright Agency of the USSR for granting the right to translate and publish.

R.J. Moseley
October, 1977

CHAPTER 1

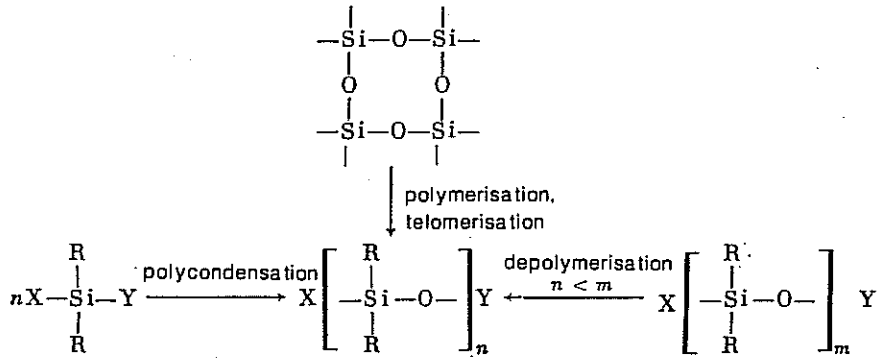
SYNTHESIS OF LOW-MOLECULAR ORGANOSILICON RUBBERS

The majority of cold-curing organosilicon compositions are based on low-molecular polymers of the general formula $HO(RR'SiO)_nH$, where R and R' are organyls (organic radicals;Transl.), differing from the analogous high-molecular compounds in the number of elementary RR'SiO units.

. To make elastic cold-cured vulcanisates it is necessary to use polysiloxanes of MM upwards of 10 to 20 thous. (1,2). The rise in the viscosity of the polymer with increase in MM restricts the maximum value for the latter, which, if we are to maintain flow and obtain vulcanisates with optimum physicomechanical properties, should as a rule not exceed 80 thous. Polymers with MM below 10 thous., even though they are very reactive and structurise readily under the action of polyfunctional derivatives of silicon, are not of interest for the production of rubbery materials, since their vulcanisates do not exhibit elastomer properties (3,4).

Bifunctional organosilicon polymers with MM in the 10 to 80 thous. range can be obtained by polymerisation of cyclosiloxanes or depolymerisation of high-molecular polysiloxanes, and also by hydrolytic, heterofunctional or homofunctional polycondensation of bifunctional diorganylsilanes and diorganylsiloxanes.

The methods of producing low-molecular elastogens may be represented as follows:



The most popular of the low-molecular polysiloxanes used for the synthesis of elastic cold-curing materials are polydimethylsiloxane-α,ω-diols. Such polymers can be obtained by several methods, but only those are put into practice which give high yields of the desired reaction products, fit in with the procedure, are easy to regulate with respect to MM, and give uniform high quality products.

One of the main methods of producing polydiorganylsiloxane-α,ω-diols is polymerisation of the corresponding cyclosiloxanes under the action of acidic or alkaline catalysts in the presence of regulators of MM.

Sulphuric acid severs the siloxane bond in cyclosiloxanes with the formation of sulphate and bisulphate end groups (5,6). These latter readily bring about further rupture of siloxane bonds in the ring and the formation of the polymer. The starting material is octamethylcyclotetrasiloxane or a mixture of cyclosiloxanes. For the polymerisation we use approx. 2 mass % of conc. sulphuric acid. The polymerisation stage is effected at room temperature in toluene, over 5 to 7 h. Then hot water, 1.5 mass %, is added to the mixture and the reaction mass is stirred for a further 15 min. After washing the polymer to neutral reaction and vacuum distilling off the toluene we obtain polysiloxanes of MM 15 to 20 thous. As shortcomings of this method we must count the need for careful washing free from the acidic catalyst and distilling off the solvent. The polymerisation of cyclosiloxanes may be catalysed also by acid salts of sulphuric acid (7).

Treatment of a rubbery polymer of MM abt. 400 thous., as obtained with sulphuric acid as the catalyst, with 90% ethyl alcohol (25% of the mass of the polymer) at 80°C for 1 to 8 h gives us polymers with MM from 13 to 50 thous. depending on the time of heating. However, the vulcanisates of these polymers exhibit insufficiently constant properties, and consequently this method is not used on a commercial scale.

For commercial production polymerisation of cyclic diorganylsiloxanes under the influence of alkaline catalysts is of the most importance (8,9).

In developing the technology of synthesis of low-molecular dimethylsiloxane rubbers we investigated the kinetics of polymerisation of cyclosiloxanes in the presence of caustic potash and water, and we established the links between the MM of the resulting polymers and the amount of regulator, between the reaction rate, the concentration of catalyst and the temperature of the process, and also with the conditions of mixing the reaction components (10). These links make it possible to decide the optimum conditions for obtaining low-molecular polydimethylsiloxanes of given MM (20 to 80 thous.) (11).

Under production conditions a mixture of oligo- and cyclo-diorganylsiloxanes is used as the starting material. When polymerisation is effected in the presence of catalytic amounts of caustic potash (12) the latter is not removed from the polymer but is bound by the addition of a small amount (0.2 to 0.3 mass %) of fine-particle silicon dioxide (11).

The polymerisation of diorganylcyclosiloxanes is of equilibrium character, and the polymers contain 12 to 18% of unreacted cyclosiloxanes (13,14). The presence of this amount of volatile products in the polymer adversely affects the properties of the vulcanisates based on it and also the economics of the process. The development of an effective mass exchange apparatus (10) for the removal of cyclosiloxanes from polydimethylsiloxane-α,ω-diols has made it possible to develop a high yield and economic process for producing polydimethylsiloxane-α,ω-diols.

As catalysts for alkaline polymerisation we may also use hydroxides of alkali metals (15), amines (16,17), quaternary ammonium and phosphonium bases (18). The addition of electron-donor agents (sulphoxides, acid amides, or ketones) makes it possible to sever the Si—O bonds in the cyclosiloxanes by water (19).

A continuous process has been worked out for producing a low-molecular polydimethylsiloxane (11) at 170—180°C in an apparatus consisting of a hollow column, into the lower part of which we feed the high-molecular polymer and steam. This design makes it possible to speed up the depolymerisation by means of powerful convection currents without mechanical mixing. To remove the reaction products from the column there was devised a means of avoiding passing steam and cyclosiloxanes over into the collector. The MM of the depolymerised polymer depends on the initial MM and the rate of feed of the steam. Polymers of MM ~40 thous. are formed. It is not possible to produce polymers of lower MM than this under these conditions. A polymer with reduced MM can be obtained by raising the pressure in the reaction zone to 0.3—0.6 MPa. Under these conditions polymers of MM 15 to 25 thous. are formed.

One particular method of producing low-molecular polysiloxanes is hydrolytic cleavage of the corresponding polymers at high temperature (11,20). In this way there have been obtained low-molecular polydimethylsiloxanes from high-molecular rubbers synthesised using an alkaline catalyst. The depolymerising agent was water (1,21) or an aqueous solution of an aliphatic amine (22). The polymerisation catalyst was a potassium (poly)siloxane-α,ω-diolate (23,24).

To produce polydiorganylsiloxane-α,ω-diols it is possible to use hydrolytic polycondensation of diorganyldichlorosilanes (25). By carrying out hydrolysis with excess water we obtain as the main reaction product a mixture of linear and cyclic siloxanes (26,27). With an insufficiency of water there are formed linear polysiloxanes with chlorine atoms at the chain ends, which are converted to polydiorganylsiloxane-α,ω-diols by subsequent hydrolysis (28). So as to create less severe conditions for the process the hydrolysis reaction can be carried out in a solvent (ether or toluene), in the presence of HCl acceptors (carbonate or bicarbonate of sodium etc.) (28).

A method has been worked out for the production of polydimethylsiloxane-α,ω-diols in the absence of a solvent by the hydrolysis of the end groups in α,ω-dichloro- or α,ω-diacetoxypolydimethylsiloxanes by means of water (29) or of aqueous solutions of the bases $KOH, Na_2CO_3, K_2CO_3, NaHCO_3, KHCO_3, Na_2SiO_3$ or NH_4OH (30), or also by means of aqueous suspensions of the carbonates or hydroxides of calcium or magnesium. To remove HCl residues in the latter case the reaction mixture is purged at 150 to 195°C with nitrogen or air. The polymers, in a yield of 87 to 94%, have a low content of volatile compounds. Regulation of the MM of the polymers is effected during the synthesis of the initial α,ω-dichloropolydimethylsiloxanes (31). In the course of hydrolysis the MM of the hydrolysis products changes only slightly.

Starting from polydimethylsiloxane-α,ω-diols of quite low MM, it is possible to obtain polymers of the required MM by thermal condensation at above 250°C under pressure, in, or without the presence of, water (3,4).

For the condensation of polysiloxane-α,ω-diols catalysts are used (acids, various salts, e.g. of tin, halogenophosphazines, esters of phosphoric or phosphorous acid, or ion-exchange resins) (32). The use of even small amounts of catalysts makes it possible to reduce the temperature of the process and shorten the duration.

Polydimethylsiloxane-α,ω-diols are being produced commercially in the Soviet Union, under the general designation SKTN, in four modifications, differing in viscosity: A, 1.5—2.5 Pa·sec (1500—2500 cP); B, 2.501—4 Pa·sec (2501—4000 cP); C, 4.001—10 Pa·sec (4001—10000 cP); D, 10.001—16 Pa·sec (10001—16000 cP) (GOST 13835—73). These polymers have the following main characteristics:

Density, g/cu.cm	0.96—1.23
MM	20000—65000
Solubility in benzene	Total
Cyclosiloxane content, in %, not above	2.5

The dependence of the viscosity η of polydimethylsiloxane-α,ω-diols on their MM is expressed by the following eqn. (33):

$$\eta = 2.8 \times 10^{-9} (M)^{2.63}$$

A nomogram for determining the viscosity of polydimethylsiloxane-α,ω-diols at various temperatures can be used in monitoring the production of the polymers and in preparing fluid compositions based on them (33).

Low-molecular polydiorganylsiloxanes used in cold-curing compositions may have on the polymer chain ends not only hydroxyl but other functional substituents as well — halogens and alkoxy-, acyloxy-, or amino groups etc. (34). These functional substituents can be incorporated either in the synthesis of the polymers or by means of secondary reactions. There are descriptions of the production of low-molecular rubbers of the general formula $X_{3-m}R'_mSi(R_2SiO)_nSiR''X_{3-m}$, where R' and R'' are alkyls, n is 10—1000 incl., m 0—2 incl., and X = Cl (35,36), OCOR (34—36), OR (37—9), NR_2 (35,36,38,39), ONR_2 (40), or $ON=CR_2$ (39,41,42), and of polymers with functional side groups (?R Transl.): OH (43), OCOR (37), OR (37), OH and OR (44), or OH and OCOR (45).

α,ω-Diacyloxypolydiorganylsiloxanes may be obtained by the reaction of diorganylcyclosiloxanes with anhydrides of acids under comparatively mild conditions, e.g. by heating to 150°C a mixture of hexamethylcyclotrisiloxane and acetic anhydride in the presence of ferric chloride (46). In the absence of a catalyst the process takes place at a higher temperature, 210 to 260°C. However, the degree of polymerisation of the resulting α,ω-diacetoxypolydimethylsiloxanes is not high enough for the synthesis of elastic vulcanisates. Their MM may be raised by supplementary condensation of the α,ω-diacetoxy derivatives at an elevated temperature.

Under still less severe conditions it is possible to produce polydiorganylsiloxanes with perfluoroacyloxy end groups (47,48), by starting with hexamethylcyclotrisiloxane and a corresponding anhydride, e.g. perfluoroacetic anhydride. The process takes place at room temperature. After holding in air with relative humidity 50% for 10 days the α,ω-bis(perfluoroacetoxy)polydimethylsiloxane acquires a viscosity at 25°C of 8.11×10^{-2} m^2/sec (81000 cSt).

Low-molecular α,ω-dichloropolydimethylsiloxanes may be produced by telomerisation of cyclosiloxanes in the presence of diorganyldichlorosilanes (21,49).

Dimethylcyclosiloxanes are severed by dimethyldichlorosilane in sealed ampoules at 250°C over a period of 3 to 5 h. The yield of telomerisation products reaches 72%. By subsequent hydrolysis these α,ω-dichloro derivatives are converted to polydimethylsiloxane-α,ω-diols (49).

There is published information on the synthesis of low-molecular polydimethylsiloxanes with amine or other functional end groups (31,32). The functional groups attached to the silicon end atoms may be replaced by other reactive groups. For instance, on interaction with water α,ω-dichlorooligosiloxanes form the corresponding oligosiloxane-α,ω-diols, while with ammonia or amines they are converted to the corresponding α,ω-diaminooligosiloxanes, and so on.

Along with polydimethylsiloxanes there have been used as a basis for cold-curing siloxane mixes low-molecular polysiloxane-α,ω-diols, containing, attached to the silicon atoms, vinyl, ethyl, phenyl or γ-trifluoropropyl groups (2), and also polymethyl-β-cyanoethylsiloxane-α,ω-diols and the corresponding α,ω-dichloro derivatives (50).

By cohydrolysis of methyl-γ-cyanopropyldichlorosilane with dimethyldichlorosilane and subsequent polymerisation of the products of this cohydrolysis in the presence of water at 40—60°C there is obtained a low-molecular polymer with viscosity 8.5 Pa • sec (8500 cP) (51).

There have been synthesised low-molecular polyorganylsiloxanes containing as one of the substituents attached to the silicon atoms a fluoroalkyl radical containing a functional group, for instance $CH_2CH_2(CF_2)_2COOC_2H_5$ (52). The $C_2H_5OOC(CF_2)_2CH_2CH_2Si(CH_3)Cl_2$ required for their synthesis is prepared by the reaction of $CH_2=CH(CF_2)_2COOC_2H_5$ with methyldichlorosilane on a platinum catalyst.

Polymerisation in the presence of alkaline catalysts does not give polysiloxane-α,ω-diols containing hydrogen atoms attached to the silicon atoms, since the Si—H bonds are broken under the influence of the alkali, with the release of the hydrogen and the formation of structurised polymers. To obtain polydimethylsiloxanes containing Si—H bonds different methods may be used (23,31). These polymers are frequently used for the synthesis of polyorganylsiloxanes modified at the Si—H bonds. For instance, they are capable of taking part in hydrosilylation with unsaturated compounds (olefins, halogenocycloolefins, derivatives of unsaturated acids etc.) (53).

Polymers containing Si—H end groups may be prepared by the reaction of polydimethylsiloxane-α,ω-diols or of their potassium silanolates with hydrosilanes of $RSiH_2X$ or R_2SiHX types, where R is an alkyl, alkenyl or cycloalkyl and X a hydrolysable group (54,55). Such polymers are in turn converted by interaction with carboxylic acids or potassium salts of these, in the presence of catalysts, into corresponding carboxydimethylpolysiloxanes.

The conditions have been worked out for the production of low-molecular polysiloxanes containing in the polymer chain, along with dimethylsiloxane units, fluoroalkylenephenylene units of type $Si(CH_3)_2C_6H_4(CF_2)C_6H_4Si(CH_3)_2$ (52).

The introduction of a carborane ring into a siloxane chain leads to polymers of exceptionally high heat resistance. Vulcanisates based on polycarboranesiloxanes maintain elastic properties even at 500°C (56). Accordingly very great interest attaches to low-molecular linear polycarboranesiloxanes, which can be produced by the interaction of 2,4-bis(chlorodimethylsilyl)-2,4-dicarba-*closo*-heptaborane-7, or of a mixture of this and 1,10-bis(chlorodimethylsilyl)-1,10-dicarba-*closo*-decaborane-10, with lower tertiary alcohols (57).

Low-molecular polysiloxanes containing epoxide groups (58) may, according to their structure, be used as a basis for easily curing compositions or as additives for the production of lubricating oils, resins and cold-curing compositions. These polymers may be produced by the reaction, for instance, of allyl glycidyl ether with a polysiloxane of the constitution $HO[(CH_3)_2SiO]_2—(CH_3SiHO)_{18}H$ in the presence of a catalyst, platinum on aluminium oxide. The epoxide-containing polysiloxane obtained thus, a viscous oil, contains 0.12% of active hydrogen and 16.3% of epoxide groups.

Graft siloxanes may be prepared, for instance, by reaction of polyalkylsiloxanes with 0.5 to 300 mass % of an unsaturated monomer of the type of vinyl halides, vinyl esters, styrene, acrylic or methacrylic acids or salts, esters or amides thereof, or vinylsiloxanes, in the presence of 0.1 to 5 mass % of radical initiators and at 50 to 250°C (59).

By way of illustration we may describe the synthesis of polyorganylsiloxane-α,ω-diols with graft styrene or butyl acrylate (60). The reaction between 4 pbm of a polysiloxane of viscosity 0.45 Pa·sec (450 cP) and 6 pbm of an equimolecular mixture of styrene and butyl acrylate in the presence of *tert.*butyl peroxide takes place at 125°C over 6 days, with a yield of 95%. Methacrylic acids (sic) may be grafted similarly to organosilicon polymers (61,62). A number of other polyorganylsiloxanes with a polymer part grafted by way of a C—C bond have been described as a basis for cold-curing siloxane compositions (63,64).

There are numerous descriptions of the modification of the polymer chain of polydiorganylsiloxanes by atoms of metals or non-metals. In a number of instances the addition to the polymer of even a small number of such hetero atoms leads to a significant change in the properties of the polymers or of their vulcanisates.

Among polyorganylsiloxanes containing hetero atoms in the main chain we find interesting properties in organozinc siloxanes, the vulcanisates of which exhibit long service life at —60°C. These are produced by heating diphenyldialkoxysilanes with anhydrous zinc acetate, in ratio 2.2 to 2.5 incl., at 200°C in 1,2,4-trichlorobenzene, with continuous removal of the ethyl acetate which is formed.

Chromium-containing polydimethylsiloxanes with Cr:Si ratio 1:600 may be produced by heating polydimethylsiloxane-α,ω-diols with chromium trioxide over a period of 18 h with raising of the temperature from 150 to 220°C. The viscosity of the polymer is 0.18 Pa·sec (180 cP) (65).

Viscous liquid aluminodimethylsiloxanes containing aluminium atoms in the macro chain (66) are produced from α,ω-dichloropolydimethylsiloxanes and freshly precipitated aluminium hydroxide.

Lead-containing polydiorganylsiloxanes (67) are formed by the reaction of polydiorganylsiloxanes with tetraacyloxyplumbanes, for instance with lead tetraacetate at 100—200°C in benzene or also without a solvent. The polymer precipitated by alcohol from solution in toluene is a colourless viscous oil containing 8.1% of lead.

One very promising development is low-molecular polysiloxanes containing not only methyl but also trialkylstannyl groups attached to the silicon atoms (68). When these polymers are used it is essential to employ organotin catalysts for cold curing.

Polymers of similar type may be obtained by the reaction of siloxanes with polyalkyldistannoxanes. Equimolecular amounts of, for instance, a polymethylhydrosiloxane and hexa-*tert.*butyldistannoxane are mixed in an atmosphere of nitrogen while being cooled. Then the temperature is raised gradually, and after concluding the reaction and distilling off the tri-*tert.*butylstannane which is formed as a by-product, we are left with colourless translucent polymethyl(tri-*tert.*butylstannoxy)siloxane.

We have certainly not exhausted all the methods of producing low-molecular diorganylsiloxanes with various atoms or groups on the ends of the macro chains or in the pendants, or also with various hetero atoms. This is confirmed by the constant publication of fresh communications on the synthesis of such polymers (69,70).

CHAPTER 2

ORGANOSILICON COMPOSITIONS

FORMULATION AND METHODS OF USE

The most widely used cold-curing organosilicon compositions are based on linear low-molecular polyorganylsiloxane rubbers of MM 10 to 80 thous., containing silanol end groups. They contain also various fillers (fine-particle silicic acid, titanium dioxide, zinc oxide, diatomite, carbonates and so forth), heat stabilisers (ferric oxide, compounds of zirconium, cadmium or copper, and so forth), structurising agents, for instance alkyl orthosilicates, and, finally, curing catalysts (amines, or salts of tin or other metals with carboxylic acids). Comparable materials produced outside the Soviet Union are frequently indicated by the letters RTV (room temperature vulcanising).

These cold-curing compositions are produced in single- or two-component formulations.

As a basis for self-curing formulations we may use, as well as polydiorganylsiloxane-α,ω-diols, organosilicon rubbers containing aluminium (71,72), nitrogen (73,74), phosphorus, titanium (72), or sulphur (75), or monofunctional polymers (76,77). Organic groups grafted to an organosilicon rubber do not prevent cold curing (40,78,79).

The presence of three or more functional groups in a single molecule of polyorganylsiloxanes makes it possible to carry out vulcanisation without structurising agents.

Siloxane rubbers suitable for single-component compositions may be prepared by prior attachment of methyldichlorosilane to polyorganylsiloxanes which contain vinyl groups, followed by vulcanisation on account of hydrolysis of the Si—Cl bond under the action of water vapour (26,80). In the majority of cases the attachment is catalysed by organic peroxides.

The vulcanising agents for single-component compositions are shown in Table 1. Self-vulcanising compositions are described also in a number of other communications (81,82).

Table 1 Vulcanising agents for single-component compositions

Vulcanising agent	Catalyst	Reference
$M^n(OR^*)_n$(M=Al, Ti, Zr)	—	83—96
$Ti(OR)_4$	$R_2Sn(OCOR')_2$	97
Products of incomplete hydrolysis of $Ti(OR)_4$	—	44
$Ti(OR)_4+[(CH_3)_3Si]_2NH+RSi(OR)_3$	—	38
Reaction products of $Ti(OR)_4+R_2Sn(OCOR')_2$	—	98
$Ti(OC_2H_5)_4+CH_3Si(OCH_3)_3$	—	87,99
$Ti(OC_4H_9)_4+(C_4H_9)_2NH$	—	100
$Ti(OSiR_3)_4$	—	101
$RSiCl_3$	—	102—105
	R'''_3N (R'''— alkyl, aryl)	106—108
$RSiCl_3+SiCl_4$	—	109,110
$RSiCl_3+Si(OR')_4$	—	111,112
$RSiCl_3+[R''(R'_2N)SiO]_n$ (n=3,4)	—	113
$RSiCl_3+R''_{4-n}Si(NR'_2)_n$ (n=2,3)	—	114

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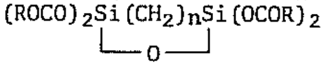
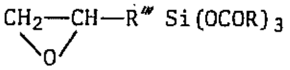
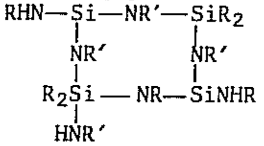
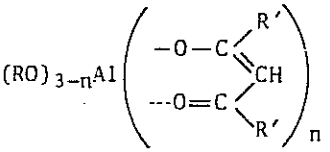
Table 1 Vulcanising agents for single-component compositions

Vulcanising agent	Catalyst	Reference
Condensation products:		
$R_{4-n}SiCl_n + R'_2C=NOH$ (n=1-3 incl.)	—	97,115–118
$R_{4-n}SiCl_n + R'_2NH$ (n=3,4)	—	119
$(R_2N)_{4-n}SiCl_n$ (n=3,4)	—	120
$R_{4-n}Si(OCOR)_n$ (n=3,4)	—	31,34,36 42,78, 121–133
$RSi(OCOCH_3)_3$	$(R''CO)_2O$ (R'''— alkyl, aryl)	134–136
$CH_3Si(OCOCH_3)_3$	$(C_4H_9)_2Sn(OCOC_7H_{15})_2$	137–140
	HCOOH, CH_3COOH	141–143
$R_{4-n}Si(OCOR')_n + R''_2OCO(R_2SiO)_mCOR''$ (n=3,4; m=10–1000 incl.)		144–146
$RSi(OCOR')_3 + R''_2Si(OCOR'')_2$ (R''— alkyl)		147–151
$Si(OCOCH_3)_4 + (RO)_{4-n}Si(OCOR')_n$ (n=0–3 incl.)	$M^n(OCOC_7H_{15})_n$ (M=Sn, Zn; n=2,4)	143–145 147–156
$CH_3Si(OCOCH_3)_3$	CH_3COOH	157
$(RO)_{4-n}Si(OCOR')_n$	—	37,82 158–160
$(RO)_2Si(OCOR')_2$	$R_{n-m}M^n(OCOR')_m$ (M=Sn, Pb, Ni, Co, Fe, Cd, Cr, Mn; n=2–4 incl.; m=0,2)	36,37 137,158 159 161–165
$(R_2N)_{4-n}Si(OCOR')_n$ (n=1–4 incl.)	—	166–168
$R_{4-n-m}(R''_2NO)_mSi(OCOR')_n$ (m+n≥3)	—	169
	—	148,170
 (R'''— alkylene)	—	120
$[R(R'OCO)_nSi]_2R'''$ (n=1,2; R''–C_1–C_4 alkylene)	—	171–173
$[R_{3-n}(R'OCO)_nSi]_2R'''$ (n=1,2; R'''–C_1–C_4alkylene)	$(C_4H_9)_2Sn(OCOCH_3)_2$	174
$RSi(NR'_2)_3$	—	175–187
$ROSi(NR'_2)_3$	—	188,189
	—	190–192
$R(R'_2N)SiO_n$ (n=3,4) (sic)	$R_2Sn(OCOR)_2$	193
$(R_2C=NO)_{4-n}Si(NR'R'')_n$ (n=3,4)	—	194,195
$[(RR'N)_3Si]_2(CH_2)_n$	—	196
$RSi(ONR_2)_3$	—	197–199
$(CH_3)_2Si[N(CH_3)C(O)C_2H_5]_2$	—	200
$(RO)_3SiNHSi(OR)_3$	—	201
$R_{4-n}Si(ON=CR'_2)_n$	—	39,41 202,203
$R_{4-n}Si(ON=CR_2)_n$ (n=3,4)	$R_2Sn(OCOR)_2$ (R–C_1–C_{17} alkyl)	41,42 204,205
$R_3SiNHCONHCOCH_3$	—	206
$(RO)_3Si(CH_2)_nX$ (X=OH, NH_2, OR, NR_2, NO_3; n=1–3 incl.)	—	207–214
$(RO)_3Si(CH_2)_nC(O)X$(X=H, NR_2; OR)	—	215
$(RO)_3Si(CH_2)_nX$ (X=H, NR_2; n=1,2)		216
$(RO)_3VO$	—	192,217

*R, R', R''— an alkyl, here and later

The curing of single-component (self-vulcanising) organosilicon compositions takes place as a rule in the presence of the atmospheric moisture. Single-component mixes may be stored for prolonged periods (from a few days to a year or more) in closed tubes or containers. They are used mainly as adhesive coatings of a few millimetres in thickness.

Vulcanisates based on single-component formulations, unlike two-component ones, prove to be adhesives, although there is so far no clear explanation for this. Among shortcomings of self-vulcanising compositions we must count the impossibility of preparing coatings of thickness above a few millimetres in a single operation. This is explained in particular by the fact that the rate of cure of such compositions is restricted by the slow diffusion of water vapour deep into the coating layer (218). This shortcoming has, however, now been largely eliminated by adding activators or by applying the coatings layer by layer. Customers also complain of the evolution of vapour of acetic acid or of amines in the curing of the compositions. Accordingly there have been found for a number of materials structurising agents which do not give off by-products of acidic or alkaline character during curing.

One of the most common catalysts, methyltriacetoxysilane, can be prepared from methyltrichlorosilane and acetic anhydride as follows (219):

$$CH_3SiCl_3+(CH_3CO)_2O \rightarrow RSi(OCOCH_3)_3+CH_3COCl$$

In addition to this, which is the simplest and least expensive method of synthesis, it is possible to use also the reaction of methyltrichlorosilane with sodium acetate (220) or of methyltris(chloroethoxy)silane (this being prepared by the reaction of CH_3SiCl_3 and ethylene oxide) with acetic anhydride (221).

In spite of an important drawback, the evolution of acetic acid in the curing of the compositions, methyltriacetoxysilane has a number of advantages as a structurising agent: its low cost, high safety, the stability of rubber mixes containing it for several months at room temperature, and also its solubility in polyorganylsiloxanes.

The amount of methyltriacetoxysilane is usually 3 to 5 pbm phr.

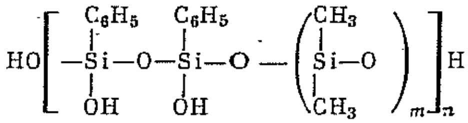
Single-component formulations, as compared with two-component, have as a rule higher adhesion, lower tensile strength, and higher elongation at break. Usually their Shore A hardness is 10 to 40, the tensile strength 1 to 2 MPa (10 to 20 kgf/sq.cm), and elongation at break 100 to 800%. Two-component formulations have the following figures: Shore A hardness 20 to 70, tensile strength 1 to 6 MPa (10 to 60 kgf/sq.cm) and elongation at break 100 to 450% (222).

Let us give an example of the employment of the Soviet single-component (self-curing) compositions KL-4, KLT-30 and KLT-50. Before using the one-component composition the surface is degreased and, if possible, sand-blasted. To improve the adhesion (particularly in the case of two-component compositions) the surface is covered with an underlayer of, for instance, K-100.

The single-component self-curing composition is squeezed out from the tube on to the surface being sealed, in a lyer 2—3 mm thick. After a certain time (usually 10 to 15 min) the squeezed-out composition loses its fluidity. At ordinary temperatures full cure is completed within 24 h. In order to improve the adhesion and physicomechanical properties it is recommended to heat treat the vulcanisate at 150 to 250°C for 24 h. To give coatings thicker than 2—3 mm the composition is applied layer by layer (a fresh layer each 24 h). The rate of cure can be increased by raising the temperature of cure to 60—70°C. Where it becomes necessary to use a more fluid composition we dilute with 'Galosha' benzine. For application by dipping we add 20 pbm of benzine to 100 pbm of the composition, with spray gun (or atomiser) we use 50 pbm of composition and 50 pbm of benzine. It is possible to use other solvents as well as these (hexane, benzene etc.).

In general, two-component compositions differ from single-component ones in the method of use. A previously prepared mixture of rubber, filler and other ingredients is mixed with the curing catalyst before use. Usually we employ 0.1—4 pbm of catalyst phr, but it is also possible to use larger amounts, which is very convenient for the user, since the curing agent does not require accurate metering and it is possible to regulate the time of cure. As a basis for two-component cold-curing organosilicon mixes we may use also a mixture of polyorganylsiloxanes containing methyl, alkoxyl or amine radicals (216).

In the majority of cases the hydroxyl groups which take part in curing at room temperature are on the ends of the molecules of polyorganylsiloxanes. However, there have appeared recently compositions based on organosilicon rubbers which have hydroxyl groups in the pendants as well. A mixture of low-molecular organosilicon polymers which contain, for each silicon atom, on an average 1 to 1.7 organic groups and upwards of 0.25 hydroxyl groups has been described. Such polymers are cured under the action of anhydrides of carboxylic acids or lead carbonate or oxide (223), or of complex compounds of copper and pyridine (224). As a component of a mix which on curing gives rubbery organosilicon materials, there may be used polysiloxanes of the following type:



$$HO\left[-\underset{OH}{\overset{C_6H_5}{Si}}-O-\underset{OH}{\overset{C_6H_5}{Si}}-O-\left(\underset{CH_3}{\overset{CH_3}{Si}}-O\right)_m\right]_n H$$

($m = 0.03 - 2.5$ incl; $n = 2 - 3$ incl.)

α,ω-Dialkoxypolydiorganylsiloxanes may be used not only in formulations which are cured at ordinary temperatures but also in heat-curing rubber mixes; this raises the tear strength from 15 to 27 kN/m (from 15 to 27 kgf/cm), and prevents premature structurisation (225).

As a dye for the widely used system of polydimethylsiloxane-α,ω-diol, ethyl silicate and stannous octoate, it is possible to add 1-N-phenylazo-β-naphthol (226,227). Using this makes it possible to judge the degree of cure from the colour change.

Vulcanising agents for two-component systems, and the catalysts, are shown in Table 2.

A number of other compositions curing like two-component systems have been described (82,228,229). As well as alkoxysilanes of the most varied structure (85,230,231), it is possible to use polyalkylalkoxysilanes as the structurising agent.

The Soviet KLSE two-component compositions are used to make solid rubbery materials of practically any desired measurements. For this purpose 100 pbm of the paste and 4 pbm of the catalyst, e.g. K-1, are mixed for 3—5 min. The resulting mixture is poured into a mould which has been prepared, or a pressure-tight part, or the like. The mixture loses its fluidity after 40 min. Complete curing takes 24 h.

One variant of two-component composition is represented by mixes which form porous rubbers by curing, or by vulcanisates obtained by hydrosilylation. The former comprise a mixture of polyorganylsiloxanes which have hydroxyl end groups with polysiloxanes which contain Si—H bonds, and a curing catalyst (amines (330), amines in conjunction with oxides of rare earth metals and diethyldicapryloxystannane (331), hydroxylamine and derivatives of it, for instance diethylhydroxylamine (332), or salts of metals and carboxylic acids (333)).

Table 2 Vulcanising agents for two-component compositions

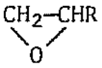
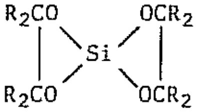
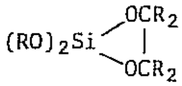
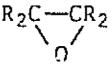
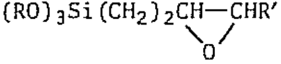
Vulcanising agent	Catalyst	Reference
$Si(OC_2H_5)_4$	$R^{*}_{n-m}M^{n}(OCOR')_{m}$ (n=2,3; M=Pb, Zn, Cd, Ti, Zr, Al, Mn, Fe; R″—(sic) C alkyl)	232—238
	$Ti(OC_4H_9)_4$	239,240
	CCl_3COOH	241—243
	$R_2Sn(OCOR')_2$	233,234 245—248
	NH_4X (X=Cl, HCO_3)	249
	$(RC_6H_4SO_3)_2Sn$	250
Products of incomplete hydrolysis of $Si(OC_2H_5)_4$	$R_2Sn(OCOR')_2$	251—256
Ethyl silicate	$R_{n-m}M^{n}(OCOR')_{m}$ (M=Zr, Sb, Fe, Cd, Ba, Ca, Ti, W(?), Mn, Li, Zn, Al; n, m=1—3 incl.)	38,159, 226,233, 255, 257—260
	R_3N and $R_2N(CH_2)_nNR_2$ (n=1—3 incl.)	261—263
	$CuCl_2 \cdot C_6H_5NH_2$	264,265
	$RR'NPX_2$, $RR'NP(O)X_2$	60,266
	$(OHC_2H_4)_2NH$, $(C_4H_9)Sn(OCOC_{11}H_{23})_2$	233,267
	$(CH_2CHNR_2)_n$ (n=10—1000 incl.)	268
	$Sn(OCOC_7H_{15})_2$	269,270
	$(CH_3C_6H_4SO_3)_nM^{n}$ (M=Zn, W(?), Zr, Ti; n=2,4)	275
	$R_2Sn(OCOR'_2)_2$	271
	$R_2Sn(Cl)OR$	273,274
	$(C_4H_9)_2Pb$	276—278
	$R_2Sn(OCOR')_2 \cdot R_2SnO$	261,279, 280
	R_3N or 	281
	$Pb(OCOR'')_2$	
	$R_{4-n}SnOP(O)(OR')_{2n}$ (n=1,2)	158,282, 283
	$[(C_4H_9)_2SnCl]_2O$ or $(C_4H_9)_2Sn(OH)Cl$	284
	$R_{4-n}Sn(ONR'_2)_n$ (n=2,4)	285
	Reaction products of $Ti(OC_4H_9)_4$+ +$(C_4H_9)_2Sn(OCOC_{11}H_{23})_2$	286
	Reaction products of R_2SnO+$(R_2SiO)_n$ (n=3,4)	287
	$NH_4Cl \cdot ROC(O)R'$	288
	$[(CH_3)_2NC(S)S]_2$	289
	$Zn(OCOC_6H_{13})_2$	100
	$M(OCOR)_2$ (M=Hg, Te, Pb,	276
	$M^{n}(CO_3)_n$ (n=2,3; M=Al, Mn, Pb, Cd, Ti, Zr)	147
 or 	NH_2SO_3H+R_3N	137
	R_3N	290—292
$R_{4-n}Si(OR')_n$	Condensation products of R_3N, $CO(NR_2)_2$+	281,293
$RSi(OR')_3$	$(C_4H_9)_2Sn(OCOC_{11}H_{23})_2$	102,258, 294—297
CH_2=$CHSi(OR)_3$	$(C_4H_9)_2Sn(OCOC_{11}H_{23})_2$	298
$(RO)_2Si(OCOR)_2$	—	158,159
$(C_2H_5O)_3Si(CH_2)_nNR''_2$(n=2,3; R‴=H, alkyl)	—	299,300 269,301
	—	302—304

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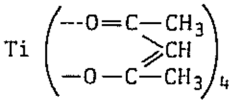
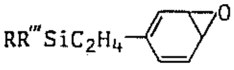
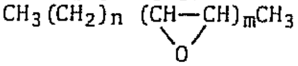
Table 2 Vulcanising agents for two-component compositions

Vulcanising agent	Catalyst	Reference
$(RO)_3SiCH_2CN$	—	305
$R_3Si(OC_2H_4)_nX_3$	$(C_8H_{17})_2Sn(OCOR)_2$	42,306
$RSi(OR')_3$ (R=H, $CH=CH_2$, OCOR″)	—	307
$RSi(OR)_3+Ti(OR)_4$	$M^n(OCOR)_n$ (M=Sb, Zn, Sn)	308
Reaction products of $RSi(OR)_3+$ $+(OHCH_2H_4)_2NH$	—	309
$[R(RO)SiO]_n$ (n=3,4)		310
$RSi(OR')_3+RSi(OCOR'')_3$	—	311
$(RO)_{4-n}Si(NR'_2)_n$	—	83,312
$RSi(NR'_2)_3$	—	313,314
$(RR'''SiO)_n$ (n=3,4; $R'''=NR_2$, ONR_2)	—	315,316
$Ti(OR)_4$	$M(OCOR')_2$ (M=Zn, Cd, R_3N)	88,317
$Ti(OC_2H_5)_4$	$(C_4H_9)_2NH$	100,318
$Ti(OR)_4$	R_2Pb	319
$Ti(OSiR_3)_4$	—	101
Reaction products of $RSi(OR)_3+$ $+(OHC_2H_4)_2NH$	—	320
$Al(OR)_3$	$R'_2Sn(OCOR')_2$	321
$(RO)_3PO$ or products of its incomplete hydrolysis	$M^n(OCOR)_n$ (n=2,3; M=Sn, Sb, Cu)	322,323
$(RO)_3B$	—	324
Reaction products of $Ti(OC_4H_9)_4+$ $+CH_3P(O)Cl_2$	—	325
Reaction products of $CH_3CH=NOH+$ $+R_2SnO$	—	326
Reaction products of $(CHOH)_5COOH+Sn(OH)_2$	—	327
 or $CH_3Si(OCOCH_3)_3$ ($R'''=C_2H_5$, C_6H_5, RO)	—	328
 $CH_3(CH_2)_n(\underset{O}{CH-CH})_mCH_3$ (n=10–1000 incl, m=2–1000 incl.)	R_3N	171,268, 329

*R, R′, R″– an alkyl, here and later

As the hydroxyl-containing components we may use OH groups which are contained on the surface of fine-particle silica (334). To obtain sponge rubbers special blowing agents may be used (335). Other methods as well have been described for making organosilicon sponge rubbers (336). The curing is rapid and may take place even at 0°C.

Compositions based on organosilicon rubbers containing vinyl groups and Si—H bonds and also catalysts, for instance platinum compounds, have elevated curing temperatures (70—100°C). These are sometimes designated LTV (see Int. Polym. Sci. Technol., 2, No. 5, 1975, p.T/76 Transl.) (elevated (sic) temperature of vulcanisation). It has recently been found possible in some cases to reduce the vulcanisation temperature to room temperature even for these. The vulcanisation of organosilicon mixes by hydrosilylation is used most where vulcanisation must not involve the formation of by-products (83,315).

As hydrosilylation catalysts we use most frequently various compounds of platinum (83,315,337—339), complexes of chlorides of platinum with phosphines (340—1), salts of platinum in conjunction with salts of bivalent tin, of mercury, bismuth or of copper (342,343). In the latter case the curing of mixtures of polyorganylsiloxanes which contain unsaturated groups with polyorganylsiloxanes containing Si—H bonds is speeded up and there is a simultaneous improvement in the life at room temperature. The platinum catalyst content is usually quite low. For instance, it is recommended that about 0.00001% of platinum reckoned on the mass of the rubber be used, the salts of tin and the other accelerators in amounts of 0.35 to 75 pbm per pbm of platinum (344,345). A number of other catalysts are used for curing by hydrosilylation (336,337,346).

To obtain translucent rubbers by cold vulcanisation there may be used, for instance, compositions consisting of polyorganylsiloxanes with vinyl or allyl end groups, of hydrosiloxanes and of platinum compounds (347). Organosilicon compositions of such types may be stored for a month.

The cold vulcanisation of block and graft polyorganylsiloxanes takes place in the same way as in the case of ordinary linear low-molecular organosilicon rubbers. They are vulcanised, for instance, by an ordinary cold vulcanisation system of structurising agent and catalyst (78,348).

High strength elastic films, of tensile strength 10 to 40 MPa (100 to 400 kgf/sq.cm), may be produced by heating, in an organic solvent, methyltriethoxysilane or a mixture of this with phenyltriethoxysilane in the presence of water (for partial hydrolysis of the alkoxy groups). Further heating of the product at 80 to 300°C, with removal of water and alcohol, does not reach the stage of gelling. Curing is carried out using ordinary catalysts of cold vulcanisation below the gelling temperature (349).

Compositions and sealants may contain not only linear polysiloxanes but also siloxane or urea-aldehyde or melamine-formaldehyde resins (234) or surfactants of the $(R_4N)Cl$ or $C_4H_9C_6H_4O(CH_2CH_2O)_{40}H$ type (350).

Paste-type compositions may be applied to a former by hand or using a spatula. Such compositions should be used only for copying deeper reliefs of surface.

The vulcanisation of two-component compositions is effected with the addition of liquid or paste-type curing agents. The type and amount of curing agent, and also the temperature of vulcanisation, determine the pot life of the composition (the time for the mix to lose its fluidity) and the curing time. A gradual rise in the viscosity of the mass of the composition indicates that vulcanisation has begun. Raising the temperature shortens the pot life and the vulcanisation time.

To produce vulcanisates with optimum physicomechanical properties it is necessary for the curing agent to be distributed uniformly within them. The mass is best mixed with the curing agent in a vessel of polymer material, preferably in vacuum, so as to avoid air inclusions in the vulcanisates. It should be taken into account that the mass will foam in a vacuum, and accordingly the vessel for the mixing must not be filled more than half full. If it is not possible to remove the air from the mixture by formation of a vacuum, it is recommended to calculate the amount of curing agent so that the vulcanisation takes place slowly. In this case the air bubbles trapped in the mixing will escape from the mass which has not been able to thicken. In any case the mixing must be effected so that as little air as possible gets into the mass.

As pigments there are used inorganic colouring agents (0.1 to 0.5%) — for reddish-brown, ferric oxide; for white, titanium oxide; for green chromium oxide. These metal oxides are at the same time effective heat stabilisers.

Materials based on organosilicon compositions can be used on site and do not require special equipment for this. They may be applied by dipping, casting, with a spatula or by spraying. It is possible to use dispersions in carbon tetrachloride, benzine or other solvents.

The underlayers used to improve the adhesion of these compositions to various surfaces are supplied in the form of dilute solutions in low-b.p. organic solvents.

They contain high heat resistance resins (e.g. siloxane) which cure, as a rule, at room temperature, methyltriacetoxysilane, etc. They have to be applied to the previously cleaned surface of the material in a thin layer, e.g. with a brush or spray, or by dipping. In the case of smooth surface (polished sheet metal) it is desirable, if the primer dries out forming an uneven surface, to apply a thin layer of the coating with a small brush to the primer before this dries out. The density of the coating of the primer depends on the absorptive capacity of the material — the higher this capcity, the thicker the applied layer needs to be. As a rule we use an underlayer which dries out at room temperature. With raising of the temperature the drying time is reduced, while in the cold it is lengthened.

For articles which have to bend, twist, compress or stretch an underlayer is not recommended, as it breaks up under such deformation. The bonded parts must be rigid. The cured siloxane composition used as the bonding layer is capable of mechanical deformation.

The underlayers used in the treatment of ceramic articles, glass, metals or synthetic polymer materials should be tested beforehand for effectiveness of adhesion under the conditions in question. The drying-out time of the underlayer varies from 15 min to 1 h depending on the absorption capacity of the material, the type of primer and the nature of the solvent. After the drying-out of the underlayer the organosilicon composition (single- or two-component) is applied.

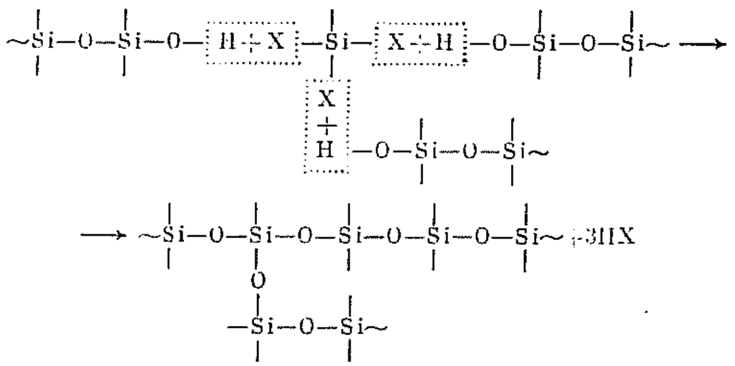
The adhesion of the primer to organosilicon compositions which contain a large amount of solvent, and the retention of the effectiveness of the primer, may be improved by a brief (10 min) additional hot drying of the already dry underlayer at 120—150°C. However, this is not always possible technically or else it brings about impermissible changes in the actual material. When the composition is applied without using an underlayer the surface of the material is prepared in the same way as when primers are being used.

CURING

The first attempts to vulcanise low-molecular organosilicon rubbers were in the early 50s. The use of organic peroxides, e.g. benzoyl peroxide, for this purpose was patented in the U.S.A. (351). However, the methods of condensation and of poly-attachment were used subsequently in the laboratory and commercially. As in hot curing of rubber mixes, peroxide vulcanisation is sometimes used for curing compositions based on low-molecular polyorganylsiloxanes (352).

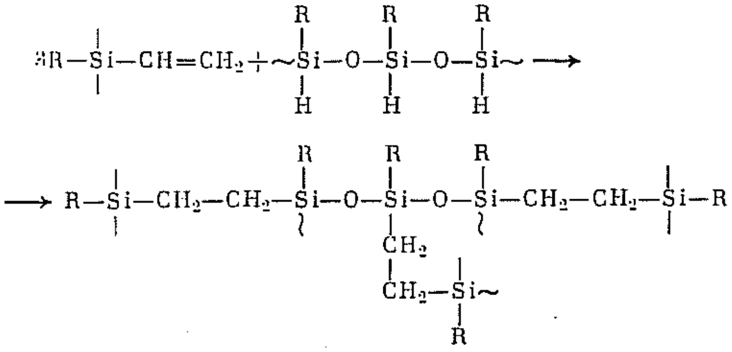
Cold vulcanisation was carried out in 1954 (353). By now the number of publications on cold vulcanisation has reached several thousand.

The curing (this term is often used as a synonym for vulcanisation) of polyorganylsiloxanes, taking place at room temperature (20—25°C), is effected in the majority of cases as follows:



Here X stands for OR,OCOR,NR_2 and other hydrolysable functional groups. The number of X substituents in the crosslinking agent has to be not less than three.

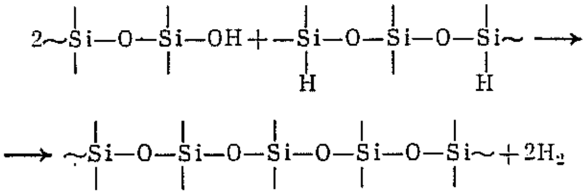
Curing may also take place by poly-attachment reactions



$$3R{-}\overset{|}{\underset{|}{Si}}{-}CH{=}CH_2 + {\sim}\overset{R}{\underset{H}{Si}}{-}O{-}\overset{R}{\underset{H}{Si}}{-}O{-}\overset{R}{\underset{H}{Si}}{\sim} \longrightarrow$$

$$\longrightarrow R{-}\overset{|}{\underset{|}{Si}}{-}CH_2{-}CH_2{-}\overset{R}{\underset{\wr}{Si}}{-}O{-}\overset{R}{\underset{CH_2-CH_2-\overset{|}{\underset{R}{Si}}\sim}{Si}}{-}O{-}\overset{R}{\underset{\wr}{Si}}{-}CH_2{-}CH_2{-}\overset{|}{\underset{|}{Si}}{-}R$$

and by dehydrocondensation



$$2{\sim}\overset{|}{\underset{|}{Si}}{-}O{-}\overset{|}{\underset{|}{Si}}{-}OH + {-}\overset{|}{\underset{H}{Si}}{-}O{-}\overset{|}{\underset{|}{Si}}{-}O{-}\overset{|}{\underset{H}{Si}}{\sim} \longrightarrow$$

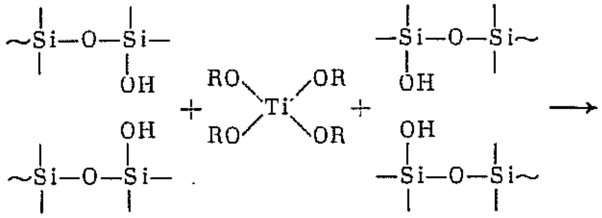
$$\longrightarrow {\sim}\overset{|}{\underset{|}{Si}}{-}O{-}\overset{|}{\underset{|}{Si}}{-}O{-}\overset{|}{\underset{|}{Si}}{-}O{-}\overset{|}{\underset{|}{Si}}{-}O{-}\overset{|}{\underset{|}{Si}}{\sim} + 2H_2$$

The reactivity of the functional groups attached to the silicon atom decreases during hydrolysis in the rating: Cl>OCOR>OR (26). This behaviour holds good also in the curing of polyorganylsiloxanes with silanol end groups using structurising agents of the $R_{4-n}SiX_n$ type, where R is an alkyl or aryl radical, $n = 3$ or 4, and X = Cl,OCOR or OR.

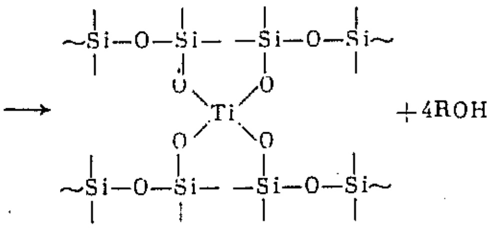
In the presence of organosilicon compounds which contain a Si—OCOR group vulcanisation takes place under the action of atmospheric moisture. The reaction is catalysed by the carboxylic acid formed in the hydrolysis of the curing agent. Accordingly the rate of cure depends to a great extent on the rate of diffusion of water vapour through the layers of the gel which is formed (218). The silanol groups, formed by hydrolysis, in the molecule of the curing agent condense with the silanol end groups of the rubber. As a result we get a rise in the MM of the rubber and formation of branched structures. The reaction takes place rapidly in the surface layer, and slows down gradually as the process penetrates more deeply.

Polydimethylsiloxanes with diacyloxy end groups make it possible to obtain vulcanisates which cold-cure under the action merely of atmospheric moisture without the addition of any curing catalysts whatever to the composition.

An investigation has been made into the vulcanisation of polyorganylsiloxanes with silanol end groups and also esters of orthotitanic acid (83). The reaction takes place at a considerable rate, apparently as follows:

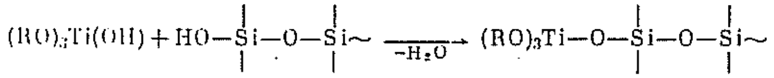


$$2\,{\sim}\overset{|}{\underset{|}{Si}}{-}O{-}\overset{|}{\underset{OH}{Si}}{-} + Ti(OR)_4 + 2\,{-}\overset{|}{\underset{OH}{Si}}{-}O{-}\overset{|}{\underset{|}{Si}}{\sim} \longrightarrow$$



The curing process is gradual, but speeds up in the presence of traces of water:

$$\mathrm{Ti(OR)_4 + H_2O \longrightarrow (RO)_3Ti(OH) + ROH}$$



$$\mathrm{(RO)_3Ti(OH) + HO{-}Si{-}O{-}Si{\sim} \xrightarrow[-H_2O]{} (RO)_3Ti{-}O{-}Si{-}O{-}Si{\sim}}$$

and so forth.

The formation of Ti—O—Si bonds in the vulcanisation is confirmed by the fact that in the IR spectra of the products of the reaction of tetrabutoxytitanium and polydimethylsiloxane-α,ω-diols of the general formula $HO[(CH_3)_2SiO]_nH$ (n = 2,3,4) there is a characteristic band at 980 cm^{-1}, ascribed to stretching vibrations of the Ti—O—Si bond. The PMR spectra show a rapid exchange of the butoxy groups of the butyl alcohol formed in the condensation and the butoxy groups of the tetrabutoxytitanium. Such an exchange does not occur between the butoxy groups of tetrabutoxysilane and of butyl alcohol (84).

Condensation of the polyorganylsiloxane-α,ω-diols and etherification of the silanol end groups by the butyl alcohol, which are side reactions accompanying the curing, take place in practice only to an insignificant extent.

The possibility of varying the nature of the functional end groups of the polymer allows the use of the most varied vulcanisation systems for single-component compositions, and also, where necessary, to avoid the formation of products of the curing reaction, for instance acids, which may have a harmful effect on materials with which the vulcanisate comes into contact.

There have been a number of investigations of the reactions of condensation of alkoxy derivatives of silicon with the silanol groups of siloxane rubbers, which form the basis of the reactions of cold curing for two-component mixtures. This type of curing reaction was first described in 1957. The interaction hardly takes place at all at room temperature in the absence of a catalyst, and begins only at higher temperatures (354):

$$\mathrm{\equiv Si{-}OH + RO{-}Si{\equiv} \rightarrow \equiv Si{-}O{-}Si{\equiv} + ROH}$$

In a number of cases, determined by the influence of the substituents in the molecules of the reagents, in particular of those containing an amino group, the condensation reaction is autocatalytic and may take place under less arduous conditions. To speed up the condensation of polydimethylsiloxane-α,ω-diols with alkoxysilanes, which is the basis of the process of cold curing, the most varied catalysts may be used (see Table 2). Salts of metals and of carboxylic acids, organic acids, and various amines, are particularly extensively used. The condensation of monomeric silanols with alkoxysilanes is speeded up by sodium silanolate (355), sulphuric acid (356), dibutyldiacetoxystannane (357) or dialkyldilauroyloxystannane (or 'dialkyltin dilaurate' Transl.) (122).

The catalytic activity of $R_2Sn(OCOR')_2$ rises with reduction in the length of the alkyl or acyl radicals. The rate of vulcanisation rises particularly noticeably with reduction in the length of the alkyl radical. The rate of vulcanisation depends to a considerable extent both on the amount of catalyst and on its nature. The catalytic activity of the tin compounds rises as follows:

$$(C_4H_9)_2Sn(OCOC_{17}H_{35})_2 < (C_2H_5)_2Sn(OCOC_{17}H_{35})_2 <$$

$$< (C_4H_9)_2Sn(OCOC_7H_{15})_2 < (C_2H_5)_2Sn(OCOC_7H_{15})_2$$

With 3 pbm of structurising agent and 1 pbm of catalyst phr the pot life of the composition is, in the presence of the system ethyl silicate-40 + dibutyldilauroyloxystannane, 22 min, of a mixture of butyl silicate-40 with the same catalyst 92 min, of a mixture of ethyl silicate-40 with dibutyldicapryloxystannane or di*iso*butyldicapryloxystannane 11 or 142 min respectively, of 2-methoxyethyl silicate-40 and tetrahydrofurfuryl silicate-40 with dibutyldilauroyloxystannane 1.5 and 26.5 min. As these examples show, butyl silicate reacts considerably more slowly than ethyl silicate. The catalytic activity of salts of carboxylic acids decreases as follows:

$$Sn(OCOC_7H_{15})_2 > Sn(OCOC_{17}H_{35})_4 > Pb(OCOC_7H_{15})_2 > Pb(OCOC_7H_{15})_4 >$$

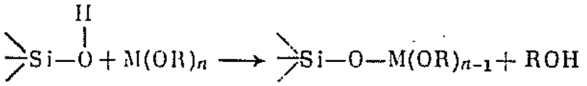
$$> Sb(OCOC_7H_{15})_3 > Zr(OCOC_7H_{15})_4$$

The rate of vulcanisation falls with partial replacement of OH end groups by R_3SiO and SH groups (358), while with a SH:OH ratio of 2:1 there is practically no structurisation (359).

The cleavage of polyorganylsiloxanes by the alcohols formed in vulcanisation using alkoxysilanes apparently does not take place at curing temperature. However, it may take place at elevated temperatures.

It had been suggested that vulcanisation at room temperature may take place both on account of silanol end groups and by rupture of the main siloxane chain. It was later confirmed experimentally that the main siloxane chain is not involved in the vulcanisation and that the functional groups on the chain ends react. In point of fact, with blocking of the silanol end groups, e.g. by trimethylsilyl groups, vulcanisation under the influence of aluminium alcoholates does not lead to the production of elastomers, and practically does not occur at room temperature (361).

Vulcanisation by means of metal alcoholates of the general formula $M(OR)_n$ takes place as follows (86):



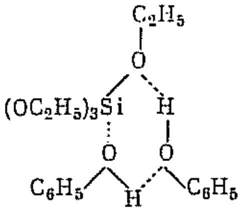
$$\rangle Si-\overset{H}{\overset{|}{O}} + M(OR)_n \longrightarrow \rangle Si-O-M(OR)_{n-1} + ROH$$

With the introduction of electron-donor compounds of amine type into the reaction zone the structurisation slows down, and at an aluminium butylate:amine ratio of 2:1 or 3:1 there is practically no reaction, apparently because of deactivation of the metal alkoxide resulting from formation of a complex of it with the amine (85).

When aluminium alcoholates are used as structurising agents vulcanisation takes place at room temperature practically instantaneously (85). This makes them inconvenient for practical use as curing agents. Since alkoxyl groups attached to atoms of tin, lead etc. are likewise too reactive, it is the acyloxy derivatives of these metals which are most used in practice. Using salts of lead or of tin and carboxylic acids vulcanisation of organosilicon compositions is achieved with as little as 0.1% of phenyltriethoxysilane. However, in practice we use a larger amount of structurising agent for practical reasons (362). It has been found that the structurisation of polyorganylsiloxane-α,ω-diols using esters of orthosilicic acid, and with dialkyldiacyloxystannanes as catalysts, takes place without any induction period.

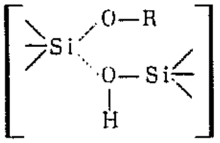
Before studying the mechanism of vulcanisation using alkoxysilanes let us briefly consider the capacity of these latter for complex formation. The tendency of the oxygen atom in the group $\equiv$Si—O—R of tetraethoxysilane to the formation of a hydrogen bond is only slight, and this substance is not capable of formation of stable molecular complexes with electron donor compounds of the organic amine type (363). This last-named situation is brought about by the low steric accessibility of the silicon atom in $Si(OC_2H_5)_4$, and also by $p\pi - d\pi$ interaction of the unshared electrons of the oxygen atom with the free 3*d*-orbitals of the silicon atom.

Compounds of type C_6H_5X, where X (?R Transl./Ed.) = OH or NH_2, form with tetraethoxysilane molecular complexes of the general formula $Si(OC_2H_5)_4.2C_6H_5R$, which apparently has a ring structure of type:

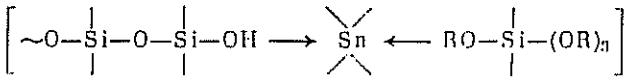


Alcohols, particularly butyl alcohols, do not form molecular compounds of the type described with tetraethoxysilane.

There is as yet no definite interpretation of the mechanism of cold vulcanisation of the system polyorganylsiloxane-α,ω-diol + tetraethoxysilane + organotin catalyst. According to Andrianov, the main mechanism suggested for the condensation of silanol and alkoxyl groups in the absence of a catalyst is attack by the silanol upon the silicon atom of the alkoxysilane. The transition complex has the following structure:



According to (362), in the first stage of the reaction there is formed the complex:

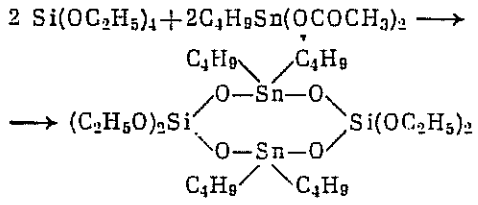


$$\left[\sim O-\overset{|}{\underset{|}{Si}}-O-\overset{|}{\underset{|}{Si}}-OH \longrightarrow \overset{\diagdown\,\diagup}{\underset{\diagup\,\diagdown}{Sn}} \longleftarrow RO-\overset{|}{\underset{|}{Si}}-(OR)_3\right]$$

With mixing of the polyorganylsiloxane-α,ω-diol with tetraethoxysilane and organotin catalyst the IR absorption spectrum of this system changes — the position of the characteristic absorption band of the silanol group shifts to 3300 cm^{-1}. The interaction takes place immediately after the mixing of the components; there is no induction period. After regrouping of this complex a polyorganylsiloxane is formed, alcohol is formed and the catalyst regenerates itself.

The alcohol formed in the reaction apparently also combines with the complex. In the reaction there is formed a polyorganylsiloxane with end groups of —O—$Si(OR)_3$ type (362), and this, by analogy with tetraethoxysilane, takes part in further reactions. With the interaction of the second alkoxyl group there is a rise in the MM, and when the third alkoxy group reacts we get structurisation of the rubber.

According to (364), in the condensation of tetraethoxysilane and an organotin catalyst there is formed an organo-tin-silicon compound, e.g. as follows:



The rate of vulcanisation is determined mainly by the rate of formation of this compound, which rate is in turn greatly affected by the polarity and three-dimensional structure of the initial organotin catalyst. The smaller the substituent attached to the tin atom the more readily it enters into reaction with the tetraethoxysilane.

The duration of vulcanisation is linked with the concentration of catalyst (362):

$$\tan\alpha = \tfrac{1}{2} \times 2.303 \log k\sqrt{C_{cat}}\,(n_{OR} - n_{OH})$$

where α is the slope of the curve on the coordinates τ_{vulc} vs. $1/\sqrt{C_{cat}}$; C_{cat} the catalyst concentration; n_{OR} the number of alkoxy groups; n_{OH} the number of OH groups; and k the characteristic of the activity of the catalyst.

This equation may be used to calculate the rate constants of the reaction of cold vulcanisation of siloxane rubbers in the presence of various catalysts.

In two-component compositions it is possible to use organosilicon structurising agents with readily hydrolysing groups attached to the silicon atom, which are typical of single-component compositions, since they may be mixed with the other components directly prior to use, although this is less convenient.

Mixtures of copolymers of polyorganylsiloxanes with other compounds, for instance with PVAL (365), or mixtures of organic and organosilicon rubbers (366), are not considered here, since the vulcanisates have relatively low heat resistance.

The choice of catalyst depends above all on the technology of using the organosilicon mix and the properties desired in the vulcanisates.

Cold-curing compositions can be used either in the mass or in solvent. For instance, polyorganylsiloxane-α,ω-diols in conjunction with an organosilicon resin, ethyl silicate (the product of incomplete hydrolysis of tetraethoxysilane) and a metal salt of a carboxylic acid may be used in a mixture with saturated hydrocarbons (benzine or hexane) (367). As vulcanisation retarders aminoalcohols may be used (368). Apparently moisture catalyses the reactions of condensation which take place in two-component compositions. With careful drying-out of all the components of the system, a polyorganylsiloxane-α,ω-diol + tetraethoxysilane + dibutyldilauroyloxystannane mixture can be stored at room temperature, without vulcanising, for more than two weeks (369).

Polyorganylsiloxanes containing Si—H bonds may be vulcanised by means of organic compounds containing more than two vinyl, ethynyl or isocyanate groups, or by means of complex compounds of Group VIII metals (370). For each Si—CH=CH_2 groups there are 0.75 to 1.25 Si—H bonds, there being one vinyl group for not less than 100 silicon atoms. It is convenient to use a platinum catalyst, prepared, for instance, by the reaction of a complex of platinum chloride with an olefin, which is heated with a vinylalkylcyclosiloxane until removal of the olefin from the reaction mixture. The new complex which is formed is thereafter used instead of the mixture of polyorganylsiloxane and platinum catalyst. The vulcanisation is carried out by means of structurising agents, i.e. organosilicon oligomers which contain Si—H bonds (395). Tetraorganyldisilazanes of the formula $(CH_2=CH)_n(CH_3)_{3-n}SiNHSiR_3$ simultaneously vulcanise the mix and lengthen its storage life (371). The use of organic compounds of cobalt, $Co_2(CO)_8$, $HCo(CO)_4$, is described in (372). The curing by means of these catalysts, used in amounts of 0.1 to 1.0 pbm reckoned on the mass of the low-molecular siloxane rubber, takes place at room temperature or somewhat above (70°C) (372). To stabilise organosilicon mixes which are cured by means of platinum compounds there are also used acetylene compounds of $(CH_3)_2C(OH)C{\equiv}CH$, $CH_3C(CH_3)C{\equiv}CH$ type. These compounds render the composition stable even when heated above 100°C. Without them a gel is formed even within 15 min under these conditions (373). The reactive vinyl groups and Si—H bonds may either be statistically distributed along the length of the molecule or be at its ends.

Compositions vulcanised by hydrosilylation are as a rule cured at higher temperatures (50—100°C). Data have recently been published on the occurrence of reaction at near to room temperatures. The compositions may be used with the employment of solvents, in particular halogenoalkanes (374).

A composition of α,ω-divinylpolydiorganylsiloxanes with platinum catalysts and hydrosiloxanes may be used (375), sometimes mixed with allylmethylcyclosiloxanes (331). The platinum compounds may be used on carriers — carbon, aluminium oxide, or asbestos (376) — in the form of salts or complexes. Such complexes are synthesised by the interaction of chloroplatinic acid with an alcohol or by heating platinum chloride with aminophosphine (343). An unsaturated component, of b.p. above 100°C, is added to the composition.

Diolefins or olefin groups may also occur on the ends of an oligomeric compound (336). There are also used α-ω-diallylpolydiorganylsiloxanes and methylallylcyclosiloxanes having only half as many allyl groups as Si—H bonds.

Cold-cured organosilicon rubbers may be produced by dehydrogenocondensation. In this case, as a rule, there are formed foam (or sponge) rubbery materials, or, if the hydrogen evolved is removed, ordinary rubbery materials. The hydrogen atoms in the hydrosiloxanes, which are of hydride character, react with various hydroxyl-containing compounds with the formation of hydrogen, and this likewise makes it possible to produce foam rubbers.

CHAPTER 3

PROPERTIES OF VULCANISATES OF LOW-MOLECULAR ORGANOSILICON RUBBERS

INFLUENCE OF FILLERS ON THE PHYSICOMECHANICAL PROPERTIES OF THE VULCANISATES

Vulcanisates of low-molecular organosilicon rubbers are essentially elastogens, since they acquire elastic properties only after curing, but up to that point are pseudoliquids (461).

The physicomechanical properties of cold-curing organosilicon rubbers depend on a whole series of factors: the structure of the siloxane macrochain, the MM of the polymer (or, more precisely, the MMD), the character and number of crosslinks, the concentration and type of filler and of vulcanising agent, the conditions of vulcanisation and so forth.

A particularly important factor is the capacity of organosilicon vulcanisates for retaining satisfactory physicomechanical properties at high temperatures. For instance, comparison of a siloxane rubber with elastomers of the types of butyl rubber, NR, EPDM, nitrile rubber, acrylic or chloroprene rubbers shows that with heat ageing in air at 161°C for 70 h only the silicone rubber and the EPDM retain their elasticity, while after this time of ageing at 225°C only silicone rubber retains its elastic properties (462).

Because of the low molecular interaction the influence of fillers on the physicomechanical properties of polysiloxane rubbers is quantitatively different from the case of general purpose rubbers. For instance, the addition of fillers to crystallising rubbers increases the strength 1.5- to 2-fold, to non-crystallising rubbers 7- to 10-fold. At the same time the reinforcement factor of siloxane vulcanisates (the factor by which the strength of the vulcanisate is raised by the addition of fillers) may be 40 or more (97).

Properties and production of fillers. There are an enormous number of publications on the methods of producing fillers — whether they are actually in use in industry or not — and accordingly we shall consider here only the main methods of producing fillers which are used to reinforce organosilicon rubbers.

Fillers generally may be divided into two main groups, silicate and non-silicate. The former includes a multiplicity of oxygen compounds of silicon, of natural or synthetic origin:silicon dioxide, metal silicates, polysilicic acids, organo(?organyl)silicates, and products of cohydrolysis of silicofunctional monomers of the type $R_{4-n}SiX_n$ ($n=1$—4; X=Cl, OR, OCOR).

The second group includes fine-particle metal powders, metal oxides and salts, various polymeric materials and so on. The fillers widely used for organic vulcanisates have not been much used for siloxane elastomers, mainly because they slow down peroxide vulcanisation and adversely affect the dielectric properties of the vulcanisates.

As to methods of production, silica fillers are best divided into natural, precipitated and pyrogenic. Silica, which is common in the earth's crust, is the basis of ordinary river sand and is found in the form of various minerals (quartz, tridymite and cristobalite) and sedimentary rocks formed by the skeletons of one-celled diatoms (diatomite, kieselguhr or infusorial earth) (310), which are of light mass and porous. These minerals and rocks contain 56 to 95% of silica, 0.1 to 10.5% of alumina, 0.2 to 10.0% of iron oxide and 0.2 to 4% of oxides of calcium and magnesium. Diatomites, frequently called diatomaceous earths, which after appropriate treatment have particle diameter in the 1 to 100 microns range, may be used as inexpensive low-reinforcing fillers.

After cleaning and comminution to particle size 3 to 100 μm ordinary sand may be used in the same way. Of such fillers the best known is the inexpensive reinforcing filler Min-U-Sil (90 dollars per tonne) with particle sizes 5, 10, 15, 30 or 75 μm (463).

Precipitated silicic acid is one of the most popular cheap fillers (464). Until recently two types were being produced in the Soviet Union, BS-50 ('white carbon black'! Transl.) and U-333. Now the range has been considerably increased (308).

The main starting material for 'white black' is sodium metasilicate (465). This is treated with chlorides of ammonium or calcium (466), sulphuric or hydrochloric acid (467), sodium bisulphite, calcium chloride and hydrochloric acid, or carbon dioxide (231). For instance, a silica filler can be produced by carbonation of an aqueous solution of sodium silicate as follows (231, 468):

$$Na_2SiO_3 + CO_2 \rightarrow Na_2CO_3 + SiO_2$$

The resulting suspension is filtered off, acidified with 10% sulphuric acid to pH 3, and the deposit washed with water to pH 6.5. Then the precipitate is dried and comminuted. In the majority of cases the diameter of the particles of powdery precipitated silicic acid shows high scatter. For instance, for U-333 this is 0.2 to 0.9 microns.

The widely used grade BS-220 is produced by precipitation of an aqueous solution of sodium metasilicate with ammonium chloride (468). Silicon dioxide of special purity can be prepared by hydrolysis of tetraethoxysilane as follows:

$$Si(OC_2H_5)_4 + 2H_2O \rightarrow SiO_2 + 4C_2H_5OH$$

followed by treatment with ammonia and calcination. Activated carbon may be used to remove micro-impurities (469). For the same purpose an aqueous suspension of SiO_2 may be purified by electrodialysis (470). A fine-particle silicic acid is produced by electrolytic decomposition of dilute aqueous solutions of sodium silicate (471). Precipitated silicic acid may also be prepared by decomposition of silicon tetrafluoride with solutions of carbonates of alkali metals (472).

Fine-particle silica may be produced by liquid phase hydrolysis of silicon tetrachloride. The process is complicated by the need to wash free of residual hydrogen chloride, and the subsequent drying and calcination of the product (465).

There are accounts of the production of this filler by pyrolysis of tetraethyl orthosilicate in house-lighting gas (473) or by oxidation of silicon tetrachloride, the chlorine evolved in the reaction being used for the synthesis of the tetrachlorosilane with which one starts (474):

$$SiCl_4 + O_2 \rightarrow SiO_2 + 2Cl_2$$

Aerosil fine-particle filler, the production of which is covered exhaustively in the literature (475,476), has proved very important for reinforcing organosilicon compositions. (Translator's Note: This trade name is used somewhat unspecifically throughout).

The first attempts to produce Aerosil from tetrachlorosilane were at the beginning of the 50s, and in 1957 Degussa began commercial production (475). Cab-O-Sil, which is produced in a similar manner, has been in production in the U.S.A. since 1958 (475).

The production of Aerosil, which is amorphous polysilicic acid of high purity, is on a large scale on account of its wide use as a thickener for paints, a stabiliser for emulsions and polymers, and a light-coloured filler for general purpose rubbers. It is used in pharmacology, cosmetics, and the leather, rubber, paint and paper industries (477), and, after further removal of micro-impurities, in semiconductor technology (478). Aerosil is used in particular in hot-curing rubber mixes. Its use in cold-curing organosilicon compositions is increasing all the time. In recent years the consumption of Aerosil amounts (including all the most highly developed capitalist countries) to 22 mill. tonnes.

To produce Aerosil one may use polyfunctional derivatives of silane, $R_{4-n}SiX_n$ (where $n = 3,4$; $X = Cl, OCOR, NR_2$ or other hydrolysable substituents). However the main, and for commercial purposes practically the sole, starting material for Aerosil is silicon tetrachloride, produced for this purpose by chlorination of ferrosilicon.

Hydrolysis of silicon tetrachloride does not give a high-grade product. Accordingly to produce Aerosil there is used the homogeneous reaction of tetrachlorosilane with oxyhydrogen gas:

$$2H_2 + O_2 + SiCl_4 \xrightarrow{\sim 1000\ ^\circ C} SiO_2 + 4HCl$$

The technology of production of Aerosil of high purity (99.8%) comprises the pyrolysis of $SiCl_4$, the agglomeration of the product, desorption of the HCl from the surface of the SiO_2 and several other stages. Large flakes are separated as they pass through the agglomeration zone (479). To remove the residues of HCl occluded by the Aerosil, this is subjected to hot air and vacuum treatment. The content of residual HCl does not exceed 0.025%. The HCl formed in the process is used to make hydrochloric acid. A high degree of purity of the initial reagents, careful regulation of the feed of the oxyhydrogen gas, homogeneity of the reaction mass, a high temperature of the process (1000°C), and the employment of other measures make it possible to produce a homogeneous product (479). The resulting spherical particles are hydrophilic, of diameter 5 to 20 nm and specific surface 50 to 400 sq.m/g. Aerosil has restricted solubility in water (150 mg/litre) and has superior purity to the silicon dioxide produced by precipitation (99.8 and 88% respectively). There are on an average $\sim 10^{14}$ particles in 1 g (480,481). Aerosil differs from other types of silicon dioxide also in having fewer hydroxyl groups on the surface (482). The spherical shape of Aerosil particles applies up to a specific surface of 300 sq.m/g (483). With further increase in the specific surface the surface of the particles cracks and their size increases somewhat. Apparently the finest-particle silicon dioxide available at present is Nyocol 215, with spherical particles of size 2 nm (484).

In addition to silicon dioxide there may be produced from the corresponding metal chlorides and oxyhydrogen gas oxides of aluminium, titanium, zirconium, iron, and others as well, which may be used as reinforcing fillers or heat stabilisers for organosilicon compositions (485).

High-activity aluminium oxide may also be synthesised by hydrolysis of aluminium alcoholates (486). Mixtures of fine-particle silicic acid with other oxides or salts, e.g. $CaCO_3$, SiO_2 or Al_2O_3 (487) are used, also mixtures of silica with calcium fluoride (488), or with sodium bicarbonate (ratio 1:0.03 to 0.119 incl.) (489), mixtures of the dioxides of titanium and of silicon, or of silicon dioxide and aluminium oxide (490), or also manganese oxide and titanium dioxide (489). The oxides of magnesium (491), of zinc or of cadmium (492), of barium (493), or of other metals (38) may be used (38). Apart from oxides or salts of metals we may add directly to organosilicon compositions for room temperature curing powders of the metals themselves: nickel (494), iron, brass, aluminium or copper. Sometimes a film of silicone rubber is applied to these powders beforehand (495).

Other fillers as well are in use: zinc carbonate (196), silicon carbide (496), boron nitride (497), disulphides of magnesium or of molybdenum, zinc chloride, oxidising agents of the type of ammonium perchlorate or nitrate (435), aluminosilicates, which are often used as molecular sieves (119), talc, microcrystalline fibres of magnesium silicate (498), PTFE (489), powdery PE containing upwards of 90% of crystalline phase, polyester fibres grouped into yarns (499), PVC of particle size below 20 microns (500), phosphorus (489), mica powder (501), various silicates including organo(?yl)silicates, and polychlorophosphazines (502).

To improve the physicomechanical properties of the organosilicon compositions we add reinforcing fillers which do not structurise them and are readily wetted by polyorganylsiloxanes. This is brought about by making the molecular properties of the surface of the filler and of the organosilicon rubber similar, or by some other improvement in the wettability of the surface of the solid phase. Good wetting also improves the dispersion of reinforcing agents in the compositions. At the present time the following methods are used extensively for these purposes: 1) the production of fillers with organic groups; 2) modification of already prepared silica fillers by chemical combination of the silanol groups; 3) by incorporating special antistructurising additives directly into the rubber mixes.

The fillers which contain organic modifying groups include polyalkyl silicates, silsesquioxanes etc. Solid polyalkyl silicates may be synthesised by electrolysis of a mixture of silicic acid, or of a salt of it, with a monofunctional alcohol. A fine-particle hydrophobic filler may be produced by reaction of sodium methylsiliconate with acetic acid (503):

$$CH_3Si(OH)_2ONa + CH_3COOH \rightarrow CH_3SiO(OH) + CH_3COONa + H_2O$$

The precipitate of polymer derived from methylsilanetriol is washed free of sodium acetate, dried and calcined. The resulting hydrophobic polymer has lasting water-repellence and does not lose its properties even on boiling in water for 10 h. Its adsorption of saturated water vapour is 0.05 cu.cm/g at the most, while the adsorption of saturated benzene vapour is 0.54 cu.cm/g. Gel of methylsilanetriol polymer may be precipitated also from a water-alcohol solution of sodium methylsiliconate by means of carbon dioxide. The hydrogel produced by co-precipitation may be used as a filler in organosilicon compositions which are vulcanised at room temperature. The products of alcoholysis of vinyltrichlorosilane by using glycols improve the reinforcing action of silicon dioxide (489). An esterified silica may be obtained by using butyl alcohol to treat a silica synthesised by the reaction of sodium silicate with sulphuric acid or by hydrolysis of silicon tetrachloride (504). Fine-particle products of hydrolysis of a mixture of di-, tri- and polyfunctional derivatives of silane, so-called poly(alkylsilsesquioxane)s and products of their modification, are described in (505). The nature of the solvents and surface-active additives (sodium salts of alkyl esters of sulphosuccinic acid) influence the size of the surface. The filler particles obtained in this way are spherical.

By chemical modification of the hydroxyl surface groups it is possible to convert the hydrophilic surface of the Aerosil into a hydrophobic, and give this filler a number of useful properties. However, it is not possible to replace all the hydroxyl groups in this way. When methanol is used to treat the Aerosil only 30% at the most of the hydroxyl groups react. The Aerosil modified with methanol is stable up to 400°C (423). The reverse action of replacement of methoxyl groups by hydroxyl takes place considerably more slowly (423). The methylation increases with rise in the degree of dehydration of the surface, which, apparently, indicates the possibility of rupture of the Si—O—Si surface bonds with the formation of hydroxyl and methoxyl groups. Aluminium oxide also may be modified by means of methyl alcohol or ethyl alcohol (506). With the treatment of Aerosil by organylhalogenosilanes its hydrated surface is screened more completely as compared with treatment by the alcohols, the degree of modification of the surface being increased by preliminary dehydration.

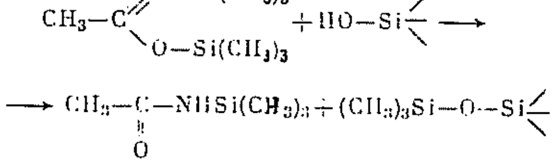
Incomplete replacement of the hydroxyl groups is indicated by the characteristic absorption bands of OD groups formed by isotope exchange of the remaining OH groups, and by a reduction in the intensity of the relevant absorption bands of the modified silica (507). This is evidence of powerful screening of the remaining hydroxyl groups by the grafted trimethylsilyl groups. With modification an interaction between the fillers and reagents may take place either on account of chemical reactions or as a result of sorption. In the former case there is a drop in the intensity of the characteristic absorption band of the hydroxyl groups which are present on the surface of the Aerosil.

Modification by means of organylchlorosilanes usually takes place at a considerable rate only above 300°C (508). Aerosil may be modified by organosilicon compounds of the R_nSiX_{4-n} type, where R is an organic radical and X a hydrolysable substituent (n = 0 to 3 incl., X = Cl, OR, OCOR or NH_2) (509,510), or by certain other organosilicon compounds (511).

Silicon dioxide may be modified by methyltriethoxysilane at 90—220°C (510). With the interaction of the hydroxyl groups on the surface with dimethyldimethoxysilane or trimethylmethoxysilane the IR absorption spectra show characteristic absorption at 2850—3000 cm^{-1}, proving the presence of CH_3 groups on the surface (510). Organylalkoxysilanes modify the surface of the Aerosil by reaction with the hydroxyl groups present on it, the alkoxysilanes reacting only with free hydroxyl groups. The stage which determines the rate of the reaction is the physical adsorption of the molecules of the alkoxysilane on the surface of the Aerosil. A description has been given of the modification of Aerosil by means of γ-aminopropyltriethoxysilane, methacryloyloxypropyltrimethoxysilane, γ-glycidyloxypropyltrimethoxysilane, γ-cyanoacryltriethoxysilane and ethyltriethoxysilane (512) (only the first of these APSs is mentioned in the source, and the ref. is given wrongly Transl.). Under these conditions there is also a reduction, or total disappearance, of the characteristic vibrations of the free silanol groups at 3745 cm^{-1} and the appearance of a characteristic absorption band for the CH_2 group at 2940—2880 cm^{-1}. After heating the Aerosil modified in this way, at 460°C, this band is reduced only slightly.

With interaction of trimethylmethoxysilane with the surfaces of silica, titanium dioxide, fine-particle amorphous boron, aluminium oxide or corundum powder trimethylsilanol and hexamethyldisiloxane are formed (173). The degree of condensation of the trimethylsilanol into hexamethyldisiloxane rises as follows: corundum < silicon dioxide < aluminium oxide < titanium dioxide < boron. With treatment of the surface of titanium dioxide which has been modified with carboxyl groups trimethylsilanol is likewise formed.

In modification with trimethylmethoxysilane, dimethyldimethoxysilane or methyltrimethoxysilane the activation energy of the reaction of these with the silanol surface groups is 92.4, 134.4 or 130.2 kJ/mol (22,32 or 31 kcal/mol) respectively. The reaction of the methyltrimethoxysilane with the silanol groups of the Aerosil goes 40% with the participation of a single methoxy group and 60% with two such groups. The third methoxy group does not take part in the reaction. Only the hydroxyl groups which are not linked by a hydrogen bond take part in the reaction. For modification we may use also organosilicon compounds containing a Si—N bond (513), including hexamethyldisilazane (514). The modification with bis(trimethylsilyl)acetamide takes place as follows (155):



$$CH_3-C\begin{matrix}\nearrow N-Si(CH_3)_3 \\ \searrow O-Si(CH_3)_3\end{matrix} + HO-Si\lessgtr \longrightarrow$$

$$\longrightarrow CH_3-\underset{\underset{O}{\|}}{C}-NHSi(CH_3)_3 + (CH_3)_3Si-O-Si\lessgtr$$

Unlike alkoxysilanes, which react with the silanol groups on the surface of the Aerosil on heating, acetoxysilanes condense with them even at room temperature (173). After treatment with organyl-acetoxysilanes there appear in the IR absorption spectrum of the modified Aerosil not only the characteristic bands of stretching vibrations of the C—H bonds, but also the characteristic frequency of a carbonyl group. This disappears after treatment of the surface with water vapour, apparently as a result of hydrolysis.

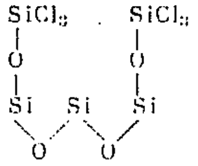
Treatment with a mixture of alkoxysilanes and octamethylcyclotetrasiloxane is described in (515).

Reactions of condensation of silane derivatives, R_nSiX_{4-n}, where X is a readily hydrolysable functional group, with silanol groups on the surface of silica may be activated with amines or tetraalkylammonium bases. To confer water-repellence there may be used also low-molecular polyorganylsiloxanes (163) or oligosiloxanes of $R(R_2SiO)_nSiR_2X(X=H, OH, Cl, OR, OCOR;\ n = 1,2)$ type. The modification of the fillers may be effected before the curing or even during it (164). In the treatment of a suspension of SiO_2 it is possible simultaneously to increase its specific surface (516). There are descriptions of the modification of fine-particle silicic acid by means of octamethylcyclotetrasiloxane (517), phenols (118), sea water, or surfactants (518).

Kaolin pigments used to reinforce organosilicon compositions may be modified by means of organylhalogenosilanes (295), while the argillaceous mineral vermiculite may be modified by means of a polydimethylsiloxane liquid (519), and the filler Santocel by means of a 10% solution of TDI.

Kaolin with a graft mercaptoorganylsilyl group — whether by itself or in a mixture with mercaptoorganylsilanes and aminosilanes — has a powerful reinforcing effect. We may note also such an exotic method of modification as the polycondensation of a polydiorganylsiloxane-α,ω-diol on the surface of fine-particle cadmium, deposited on a cathode (520).

It is possible to graft trichloro- or trimethylsilyl groups to the surface of Aerosil (521). At 250°C silicon tetrachloride reacts with silanol surface groups within a few minutes. As a result there are formed on the surface groups of the following type:



Further reaction with methyl alcohol at room temperature gives a dense trimethyoxysilyl coating. The reaction takes place within a few minutes. Each trimethoxysilyl group may act as an adsorption centre for one molecule of methyl alcohol. With prolonged contact of water vapour with a trimethoxysilylated surface of Aerosil there is substitution of hydroxyl groups for the OCH_3 (522). After reaction of the silanol surface groups of various silica-silicate fillers with organylchlorosilanes of the $X(CH_2)_mSi(R)_nCl_{3-n}(X = RCOO, N\equiv C;\ R = \text{alkyl}, Cl;\ m = 1,2,3;\ n = 0,1,2)$ type, the functional groups, X, may be used for further chemical conversions (523). Ester or nitrile groups may be converted to carboxyl groups under the action of a mixture of mineral acids and acetic acid. The nitrile groups may likewise be reduced to amino groups by means of lithium aluminium hydride, while the ester groups can be converted into hydroxyl groups by a mixture of methyl or butyl alcohol and butyl orthotitanate. Monomolecular polyorganylsiloxane coatings containing nitrile, carboxyl, ester or amino groups may be produced on the surface of quartz (524).

Commercial methods of modification of fine-particle silica of the Aerosil type are based on the reaction of silanol groups with dimethyldichlorosilane (102,256). Dimethyldichlorosilane may be used to modify, in particular, Degussa's widely used Aerosil R-972. The process is completed by desorption from the surface of the Aerosil and neutralisation of the HCl which is formed. The initial Aerosil contains about 3% of water. Accordingly in its modification a considerable amount of dimethyldichlorosilane is used and a water-repellent film is formed on the surface.

The incorporation of modifying additives directly into rubber mixes is used mainly for hot-vulcanisation compositions. However, in a number of cases this method is applicable for cold-curing compositions as well; we may note the use for this purpose of Pinakon organosilicon esters (526), diorganylsiloxane-α,ω-diols and diorganylsilanediols (527), a mixture of diphenylsilanediol with hexamethyldisiloxane (365), alkoxysilanes and siloxanes (528,529,530), esters of dicarboxylic acids (531), triethylamine (532), ammonium bicarbonate (509), esters of carbonic acid (532), or boron siloxanes (37,161). The antistructurising action of diorganyldialkoxysilanes decreases in the following order:

$$CH_3(C_6H_5)Si(OCH_3)_2 > CH_3(C_6H_5)Si(OC_2H_5)_2 > (C_2H_5)_2Si(OC_2H_5)_2 >$$

$$> (CH_3)_2Si(OC_2H_5)_2 > (C_6H_5)_2Si(OC_2H_5)_2 >$$

$$> (C_6H_5)_2Si(OCH_3)_2 > (CH_3)_2Si(OCH_3)_2$$

The optimum dialkyldialkoxysilane: Aerosil ratio is 1:(3.5—5). The antistructurising effect depends on the chemical activity of the alkoxy group and the character of the organic radical linked to the silicon atom, which has a screening effect.

The important parameters of fine-particle fillers which are used in organosilicon cold-curing compositions are their specific surface, the chemical affinity with the siloxane rubbers used as a base, the porosity, the presence on their surface of functional groups and modifying compounds which are linked to the surface by adsorption or chemically, the particle fineness, and the acidity or alkalinity of the surface. The particle size distribution is non-identical even for fillers with identical chemical composition, and depends on the method of production. The specific surface is determined most frequently by low-temperature adsorption of inert gases (349).

The silanol groups on the surface on one of the most important fillers, Aerosil, are determined by chemical methods based on the reaction with B_2H_6 (145), RMgX (534), diazoethane (146), $SOCl_2$, or Ca, and also by means of IR spectroscopy (535). Methods have been developed for accelerated determination of the specific surface (536). Aerosil has a non-porous structure, while U-333, BS-220 and BS-280 have porous structures.

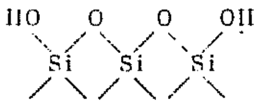
Unlike crystalline cristobalite and quartz, Aerosil has an amorphous structure (535). The refractive index of pure silicic acid (sic), n_D^{20}, = 1.452. Accordingly dispersions of it in compounds having the same refractive index (e.g. glycerol, carbon tetrachloride or various polyorganylsiloxane rubbers containing alkaryl groups) are transparent. In an electric field the negatively charged particles of the Aerosil move towards the anode.

Definite information as to the structure of the surface of fine-particle powders, and their interaction with polyorganylsiloxanes and other components of organosilicon compositions can be obtained by IR spectroscopy.

In the IR spectrum of Aerosil there is a wide absorption band in the 2800—3750 cm^{-1} region, corresponding to characteristic vibrations of adsorbed water and silanol groups which are linked by hydrogen bonds; there is also a narrow absorption peak at 3750 cm^{-1}, which is usually ascribed to free hydroxyl groups (537, 538). On the surface of heavily hydrated silicas there are in the main interlinked hydroxyl groups (539). The IR spectra of certain other fillers used in cold-curing compositions, for instance aluminium oxide and titanium dioxide, likewise contain the characteristic absorption bands of hydroxyl groups. After heat treatment in vacuum of aluminium oxide the IR spectrum still retains the characteristic absorption bands of non-perturbed hydroxyl groups at 3698, 3737 and 3795 cm^{-1} . After deuteroexchange these shift respectively to 2733, 2759 and 2803 cm^{-1} (540). In the spectrum of various modifications of titanium dioxide which have been heated in vacuum there are characteristic absorption bands of hydroxyl groups at 3675 and 3350—3100 cm^{-1} .

OH groups in silica are mainly on the surface of the particles, since they are easily replaced under the action of D_2O by OD groups (436), and, as follows from the investigation of the IR spectra, the particles are capable of sorbing argon or nitrogen on the surface. With effective dehydration the characteristic bands of the hydroxyl groups become very narrow, which is evidence of the absence of mutual perturbation of these groups (423).

The concentration of isolated hydroxyl groups with a characteristic absorption band at 3750 cm^{-1} is, after heating at 2.65 × 10^{-3} Pa (2 × 10^{-5} mm Hg) to 500°C for 3 h, 0.48 mol (?mmol) per g of silicon dioxide. Thus, as a statistical mean, one silanol group occupies an area of 0.5 sq.nm, the distance between the atoms of oxygen in the HO groups being 0.7 nm (482,521,524). Since the Si—O bond has a length of 0.164 nm, while the angle of the Si—O—Si is 105°, the arrangement of the hydroxyl groups on the heat-treated surface of Aerosil may be represented as follows:



This means that even after heat treatment in vacuum each second atom of silicon which is present on the surface of the Aerosil particle will be linked with a hydroxyl group.

In Aerosil of specific surface 200 sq.m/g one particle contains about 2000 silanol groups (349).

In the spectra of Aerosil modified with trimethylchlorosilane the characteristic absorption band of free silanol groups is absent, but characteristic absorption frequencies of a methyl group occur in the 2970 and 2915 cm^{-1} regions (538).

Important information may be obtained by studying the thermograms of the fillers used in organosilicon mixes. On the thermogram of unmodified A-380 Aerosil an endo effect at 490°C corresponds to removal of sorbed and chemically combined water. On the thermograms of previously calcined Aerosil the endo effect is less. For modified AMP-35-W-2 Aerosil a low intensity exothermic peak may be explained by oxidation of the organic surface groups and decomposition of the modifying compound (541).

Mechanism of the reinforcement of rubbers by fillers. The physicomechanical properties of polysiloxane elastomers, particularly the tensile strength, elongation at break, hardness etc., depend largely on the interaction of the components in the polymer + filler system (542). Nevertheless, in spite of the many investigations into the influence of fillers, in particular the very widely-used fine-particle silicic acid, on the physicomechanical properties of siloxane rubbers, and in spite of a number of important practical achievements in this field, many points remain obscure.

According to present ideas, there are two different types of bonds in unfilled vulcanisates (534,544): simple covalent polymer-polymer crosslinks and effective crosslinks brought about by entangled polymer structure. In the filled vulcanisates there are filler-polymer covalent bonds, and effective filler-polymer bonds brought about by the action of polar or van der Waals forces, and, finally, apparent filler-polymer bonds, formed as a result of wetting of the surface of the filler by the polymer. The mechanical properties of the vulcanisates depend not only on the number of crosslinks, but also on the nature of the filler-polymer bonds.

Nevertheless it is very difficult to consider the influence of the types of bonds which are formed on the reinforcement and physicomechanical properties of organosilicon rubbers, since the quantitative contribution of each type of interaction, and, often, even the nature and character of the intermolecular forces are not clear (545).

The interaction between silica fillers and siloxane rubber is governed above all by the sorption processes. Aerosil has powerful adsorption properties, those towards polydimethylsiloxanes included (546). The higher heats of adsorption of linear polyorganylsiloxanes as compared with cyclic may be explained by the possibility of condensation of α,ω hydroxyl end groups with the OH groups on the surface of the silica. The actual heats of adsorption are quite high, which is evidence of considerable energy of interaction. In the adsorption of polyorganylsiloxanes of MM 10000 by Aerosil (spec. surface 300 sq.m/g) or 'white black' (spec. surface 100 sq.m/g) from solution in hexane, there are formed on the surface of the filler complex configurations of molecules of the polymer, interwoven into two or more layers (546). The extent of the Gibbs adsorption of the two fillers is closely similar. The thickness of the adsorption layer reaches 1.78 and 1.51 nm with concentration of the polymer 30 mg/litre, or 1.04 and 1.25 nm with concentration 3 mg/litre. The adsorption of polyorganylsiloxanes of MM 350000 reaches a maximum quite rapidly even at low concentrations of the polymers (547). Dehydration of the surface of Aerosil which has been heated at 800°C has practically no influence on the rate of adsorption. Modification of the Aerosil with trimethylchlorosilane reduces the surface energy, since the molecules being adsorbed are displaced outwards from the surface of the silica by the thickness of a layer of trimethylsilyl groups, which have low energy of interaction (548).

With increase in the MM of the polymer its adsorption on a silicate filler increases. The presence of water in the solvent reduces the adsorption of the polyorganylsiloxanes, apparently as a result of the driving out of the macromolecules of the polymer by the molecules of water, which are capable of forming hydrogen bonds with the silanol groups on the surface of the Aerosil (549). A molecule of polydimethylsiloxane of MM 400000 occupies an area of 600 sq.nm, while the average surface of a particle of Aerosil is 800 sq.nm. Thus, the areas of the molecules of polymer and Aerosil are approximately identical. As a result the particle of Aerosil may be enveloped by a single molecule of organosilicon elastomer. It is known that the macromolecules of the latter are in the form of globules which make contact with each other and with the particles of filler only in separate portions (or segments). But the above observations indicate the possibility of unwrapping the molecule or at any rate the part of it which comes into the field of action of adsorption forces, and of the formation on the surface of the reinforcing powders of an adsorption layer of molecules with thickness τ, in nm:

$$\tau = \frac{V_m}{\omega} = \frac{640}{600} \approx 1$$

where V_m = 640 cu.nm, the volume of a molecule of polydimethylsiloxane; and ω = 600 sq.nm, its area.

Thus, the calculated adsorption layer thickness is 1 nm, i.e. practically equal to the thickness of a stretched out molecule of polydimethylsiloxane, 0.7 nm (as calculated from a van der Waals model). Certainly such a system differs significantly from actual organosilicon compositions, which, as a rule, do not contain any solvents. Nevertheless these data are evidence in support of the presence, in the adsorption field of particles of filler, of straightened-out and ordered macromolecules of polymer, which form a monomolecular layer.

The water which is always present in actual organosilicons likewise takes plart in structurisation. The particles of silica interact with each other through the hydroxyl surface groups and the water which is sorbed on the surface (550). The thixotropic properties of the 'white black' + polyorganylsiloxane system reach a maximum at water content 8%. This is quite close to the moisture content of the commercial 'white black' U-333 (not above 6.5%), and corresponds to a monolayer of water on the surface (550). With further rise in the moisture content the thixotropy decreases, apparently on account of the formation of monolayers of water on the surface. The thixotropy of a system containing calcined silica has no well-developed maximum. If we consider the strength as a function of the interaction of the particles through a layer of sorbed moisture (550), then the absence of this moisture is bound to reduce markedly the possibility of interaction of the filler particles. With low moisture content the viscosity of the system increases with time. With rise in the moisture content the water partly.diffuses from the surface with time and the viscosity of the organosilicon rubber + filler system decreases (550).

The binding of the rubber with the fillers is not simple adsorption, but includes chemisorption and mechanical interaction by entanglements of the chains of the polymers (551). For organosilicon polymers this last factor is less important than for general purpose rubbers. For instance, the MM of the sections of the chain of polydimethylsiloxane rubber between neighbouring attachments is about 15000, for ethylene-propylene rubber less than 2000.

The hydroxyl groups of the Aerosil may on account of condensation link with the silanol end groups of the polyorganylsiloxane-α,ω-diols (552).

The hydrodynamic viscosity η of a polyorganylsiloxane + filler system changes according to the equation (553):

$$\eta=\eta_{\mathrm{exp}}^{k\phi} \quad \text{(sic)}$$

where ϕ is the volume proportion of filler; k a coefficient depending on the character of the filler surface.

The formation of a thixotropic gel of the system non-polar rubber + Aerosil is on account of the linking of the particles of filler by hydrogen bonds into a three-dimensional structure (polar liquids interact less strongly). In vulcanisation there is in addition to the formation of three-dimensional polymer network, a process of cyclisation, which is characteristic of polydiorganylsiloxanes. As a result there is formed a microgel structure with higher density, linked only slightly with the rest of the polymer (288).

The specific surface of the filler is one of the most important characteristics determining its reinforcing capacity. With increase in the specific surface of the filler there is a rise in its reinforcing properties. This applies both to fine-particle silicic acids and to other powders which have a large specific surface, e.g. fine-particle aluminium oxide (485). With larger particle size we get higher filling. With identical degree of filling by means of powders those with higher specific surface give compositions with the poorest flow. For instance, a composition containing 20 pbm of $MgCO_3$ is thixotropic, while one containing 40 pbm of kieselguhr retains good flow. With the addition of 70 pbm of titanium dioxide the viscosity of the composition is 20 Pa·sec ($2 \times .10^4$ cP) (554). Of the fillers in question it is $CaCO_3$ and TiO_2, which have large particle size, which give the best flow. Aerosil, like ordinary 'blacks', apparently brings about reinforcement as a result of the formation of chain structures (536).

Light scattering and electron microscope methods have been used to show that the filler is dispersed within the polyorganylsiloxanes in a fairly complex manner. Aerosil forms agglomerates measuring a few micrometres and consisting of 40 to 50 initial particles (555). The reinforcement is linked with the energy which is necessary to breakdown the agglomerates thus formed, but nevertheless the presence of large aggregates of Aerosil may bring about a low tensile strength of organosilicon rubbers (491). Thus, a consideration of the mechanism of polymer-filler interaction shows that to form an optimum network of reinforcement of cold- or hot-curing silicone rubber mixes we need fillers with large specific surface which are capable of interaction with the organosilicon polymer.

In this direction it is the hot-curing rubbers which have been investigated most extensively. It has been found that with increase in the content of Aerosil there is improvement in the tensile strength and flexing resistance and in the elongation at break. At the same time the hardness increases practically linearly, while the other properties rise to a maximum, after which they fall. The tensile strength and the elongation at break are higher with the addition of Aerosil 300 or the hydrophobic Aerosil R-972 than with the addition of diatomite or precipitated silicic acid.

The same behaviour applies with compositions curing at room temperature. For these we investigated the influence of $MgCO_3$, $CaCO_3$, MgO, Al_2O_3, ZnO, TiO_2, Fe_2O_3, of the comminuted glasses MK-60, MK-120, MK-180 and of various grades of silica (83,556). We get the best mechanical properties in mixtures with silica or comminuted glass — fillers which come nearest in nature to the polyorganylsiloxane rubbers in question.

Inactive and low-activity fillers are frequently used in conjunction with active fillers, to reduce the cost of organosilicon compositions or to increase the hardness of vulcanisates based on these (556). Cold-curing compositions produced in and outside the Soviet Union usually contain kieselguhr, whiting, precipitated sodium (?calcium) carbonate, zinc or titanium oxides, ferric oxide, precipitated silicic acids and so on (554).

High-activity fillers of the Aerosil type are used less frequently for cold-curing compositions, since they reduce the flow of the mix even in comparatively small dosages. However, modified fillers can be added to potting compositions and sealants in much larger amounts. This makes it possible in a number of cases to obtain vulcanisates which in tensile strength, elongation at break, tear resistance and certain other properties are practically equivalent to hot-curing silicone rubbers.

With raising of the MM of polyorganylsiloxanes from 10000 to 70000 the strength of vulcanisates based on them (with identical degree of filling, of course) is likewise raised (218,554). However, for practical reasons we use in such compositions, as a rule, polymers of MM 20000 to 50000, which corresponds to viscosity 100—1000 Pa·sec (1000—10000 P). With raising of the MM within these limits the elastic and cohesion properties of the vulcanisates change more markedly than for rubbers with higher MM.

The nature of the side groups (CH_3, C_2H_5, $CH_2{=}CH$, C_6H_5, $NCCH_2CH_2$, $F_3CCH_2CH_2$ etc.) in the polyorganylsiloxanes in question has no marked influence on the elastic or cohesion properties of the vulcanisates. The incorporation of a small amount of trifunctional polyorganylsiloxanes improves the physicomechanical properties of silicone rubbers (557).

The incorporation of certain hetero atoms, for instance of titanium (401), in the polysiloxane chain, and also the use of ketoxime groups, $—ON{=}CR_2$, on the ends of the molecules of polyorganylsiloxane rubbers (558) increases the strength of organosilicon vulcanisates. Polyorganylsiloxanes containing Si—S—Si groups are similar in elastic properties to ordinary ones, but are superior to organosilicon rubbers with $Si—CH_2—Si$ groups (75).

The elasticity and strength of the vulcanisates depend also on the rate and temperature of cure and the amount and type of catalyst employed. Speeding up vulcanisation apparently does not harm the physicomechanical properties, if at the same time we do not disturb the optimum vulcanisation network and there is timely diffusion of the volatile compounds (acetic acid, ethyl alcohol, water etc.) which are evolved as a result of polycondensation reactions in the vulcanisation.

As already indicated, in the vulcanisation of polyorganylsiloxane-α,ω-diols by polyfunctional derivatives of silane, condensation products are evolved and there are reactions leading to a rise in the MM and to gel formation. In the case of polymers with low MM the former process is predominant, while with high MM it is mainly the latter which takes place.

With raising the concentration of vulcanising agent there is a fall in the strength of the vulcanisates; for instance, where the vulcanising agent is 3 or 20 pbm of methyltriacetoxysilane the tensile strength falls from 3.3 (33) to 1.5 MPa (15 kgf/sq.cm) and the elongation at break from 160 to 55%, while the Shore A hardness rises somewhat, from 50 to 60 (556). A high concentration of catalyst leads to the formation of a dense network, which slows down the diffusion of water vapour from (sic) the air and reduces the rate of cure. With a low dosage there is formed at first a sparse network, which promotes easy diffusion of water vapour. A perceptible reduction in the strength with high concentration of catalyst may be explained by reactions of dimerisation and cyclisation of the structurising agents, and by the formation of short segments of chain between the vulcanisation nodes. With alteration in the nature of the substituent in organyltriacetoxysilanes, $RSi(OCOCH_3)_3$, the vulcanised composition acquires the following properties (556):

R	CH_3	$CH_2=CH$	C_6H_5
Tensile strength			
MPa	2.9	3.3	2.4
kgf/sq.cm	29	33	24
Elongation at break, %	250	150	170
Shore A hardness	50	54	45

HEAT AND LOW TEMPERATURE RESISTANCE

One very important feature of organosilicon rubbers is the possibility of using them in the temperature range from —60 to 250°C, and in certain cases even at higher or lower temperatures than these. This is determined above all by the structure of the molecules of the polyorganyl-α,ω-diols, $HO(R_2SiO)_nH$, which occupy a place intermediate between organic and inorganic polymers. The high energy of the Si—O bond, 418 kJ/mol (102 kcal/mol) (377), ensurès good heat resistance not only in inorganic polymers of the type of quartz, but also in organic polymers, polyorganylsiloxanes, in which $R=CH_3$, C_2H_5, C_6H_5, $CF_3CH_2CH_2$, $NCCH_2CH_2$ etc. This is also promoted by the high energy of the bond Si—C, 311 kJ/mol (74 kcal/mol). The macromolecules of organosilicon rubbers interact only weakly with each other, which promotes retention of the flexibility and elasticity of the material at low temperatures and reduces the glass transition temperature. Organosilicon rubbers vulcanised by a non-peroxide method, e.g. using a cold-curing system, are more heat stable, since in their structure the crosslinks $\rightarrow$Si—C—Si$\leftarrow$ or $\rightarrow$Si—C—C—Si$\leftarrow$ are replaced by the more heat resistant $\rightarrow$Si—O—Si$\leftarrow$ (378).

The temperature of thermal and thermooxidative degradation of polyorganylsiloxane rubbers and of their vulcanisates depends on their structure and on the nature of the substituents attached to the silicon atoms (379). The thermomechanical properties of organosilicon vulcanisates depend also on a whole series of other factors, particularly on the presence of impurities or residues of catalyst, and also on the stabilisers (compounds of variable-valency metals, heterosiloxanes, compounds containing conjugated double bonds, etc.). The degradation of polysiloxane rubbers and of their mixes follows differing courses according to the actual service conditions. As a rule, the resistance of organosilicon vulcanisates is higher under atmospheric conditions than in an enclosed volume. This is explained by compensation for the breakdown of the polyorganylsiloxanes by oxidative crosslinking (380).

With heating of polydimethylsiloxanes at 200—250°C in the presence of oxygen there are basically three reactions: oxidation of the hydrocarbon groups, depolymerisation of the siloxane chain, and structurisation. The oxidation is accompanied by the formation of new groups, →Si—O—Si←, in the places of detachment of methyl groups. Thus, since in thermal decomposition of polyorganylsiloxanes there is, in addition to the oxidation of the side groups, degradation of the main chain, thermooxidation is made up of two opposing processes: breakdown of the →Si—C— and →Si—O— bonds and the formation of new siloxane bonds. The rate of these processes depends on the structure of the polyorganylsiloxanes, on the presence of additives which reduce the rate of thermooxidation, on the temperature, on the time of exposure, on the oxygen concentration, and on a number of other factors. Of course, in the service of organosilicon vulcanisates the processes are at different rates. If the thermooxidation of the side groups is predominant, then the organosilicon vulcanisate is structurised, which leads, as a rule, to reduction in elasticity. In particular, there is a reduction in the elongation at break and some increase in the tensile strength. If on the other hand the rate of degradation is the higher, the vulcanisate becomes softer, and the elongation at break increases somewhat, but the strength falls. Processes of this kind are non-characteristic of general purpose rubbers and vulcanisates. The presence of an induction period of thermooxidation in polyorganylsiloxanes, the passivation of this by compounds which act as electron traps, and certain other facts point to the radical character of this process (381). At present this point of view is generally accepted.

The oxidation of the methyl and other alkyl groups in the polydiorganylsiloxane chain takes place with the formation of carbon dioxide, carbon monoxide, formic acid, formaldehyde, methyl alcohol, water, hydrogen and various other substances (382). The primary volatile product of the oxidation of the methyl groups is formaldehyde. Along with the oxidation products a mixture of cyclosiloxanes is formed as a result of depolymerisation.

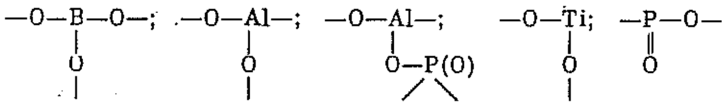
With the detachment of alkyl groups linked to the silicon there is apparently formed a Si—OH group, which is detected by means of the IR absorption spectra (383). With decomposition of these groups there may be both cyclisation with the formation of cyclosiloxanes and also condensation of the macromolecules with increase in the MM. If these groups are remote from each other and in the middle of the chain, they condense with analogous groups in neighbouring macrochains, and in this way a gel is formed. The ratio of the number of cross-links formed to the number of methyl groups split off in the initial period of oxidation is 0.02, and it subsequently rises to 0.3 with 12% of split-off $\mathrm{CH_3}$ groups. This means that in thermooxidation the formation of intramolecular siloxane bonds predominates.

The Si—$\mathrm{CH_3}$ bond is more resistant to oxidation than the Si—$\mathrm{C_2H_5}$. This is explained by the reduced resistance to thermooxidation of the methylene group in $\mathrm{CH_3CH_2Si}$. Replacement of some of the methyl groups by phenyl improves the resistance to thermooxidation.

As a result of thermooxidative degradation at 400°C of siloxane rubbers containing methyl and 3,3,3-trifluoropropyl groups, there are formed dimethylcyclosiloxanes and methyltrifluoropropylcyclosiloxane (243). At the same time trifluoropropyl groups are split off (384). This reaction is accompanied also by γ-decomposition — an intramolecular migration of atoms of fluorine from the hydrocarbon group directly to the silicon atom (110). The actual process of thermooxidative degradation begins to occur at a perceptible rate at 250°C and above, the trifluoropropyl groups being split off more rapidly than the methyl. The kinetic curves expressing the process of thermooxidative degradation are, as with the thermooxidation of polydimethylsiloxanes, S-shaped (385). This fact, and also the induction period of the process, are evidence of the autocatalytic and radical character. The intermediate products of thermooxidation are not compounds of peroxide character but aldehydes (385); for instance, formaldehyde is often detected in the oxidation products. In the products of oxidation of poly(bis-γ-trifluoropropylsiloxane) there are trifluoropropane, trifluoroethane and trifluoromethane. In addition to the volatile cyclosiloxanes a perceptible amount of gel is formed. The 3,3,3-trifluoropropyl and 2- and 3-cyanoalkyl groups reduce the resistance of the vulcanisates to thermooxidation.

In high temperature oxidation of polymers having organylsilsesquioxane units there is degradation only of the organic groups; in this case the main siloxane chain is not broken.

The incorporation of Al, Sn, Ti, P, B and other hetero atoms improves the resistance to thermooxidation of the methyl and ethyl groups linked to the silicon atoms (214,386,387). The rate of detachment of the phenyl and vinyl radicals increases according to the nature of the metal: Ti< Sn< Al. However, if the content of these hetero atoms in the macrochain is raised above an optimum the rate of thermooxidation begins to rise. There are descriptions of the incorporation into the siloxane chain of atoms of boron, aluminium, titanium or phosphorus in the form of the units (388,389):



$$-\mathrm{O}-\underset{\substack{|\\ \mathrm{O}\\ |}}{\mathrm{B}}-\mathrm{O}-;\quad -\mathrm{O}-\underset{\substack{|\\ \mathrm{O}\\ |}}{\mathrm{Al}}-;\quad -\mathrm{O}-\underset{\substack{|\\ \mathrm{O-P(O)}\\ /\ \backslash}}{\mathrm{Al}}-;\quad -\mathrm{O}-\underset{\substack{|\\ \mathrm{O}\\ |}}{\mathrm{Ti}};\quad -\underset{\substack{\|\\ \mathrm{O}}}{\mathrm{P}}-\mathrm{O}-$$

and so on.

The heat resistance of polymethylphenylphosphino(phosphono? Transl./Ed.)siloxanes (Si:P = 200:1) is noticeably higher than that of polymethylphenylsiloxanes. The resistance to thermooxidation of polyorganylsiloxanes rises with the incorporation of >P(O)O— groups (390). This is confirmed by the higher energy of rupture of the >P—O— bond, 391 kJ/mol (145 kcal/mol), as compared with that for the >Si—O— bond, 311 kJ/mol (118 kcal/mol) (these kinetic data are suspect Transl./Ed.) (387). The simultaneous incorporation of atoms of aluminium and of phosphorus into polyorganylsiloxanes improves the heat resistance and thermomechanical properties of the vulcanisates (380).

α,ω-Dichloropolydiorganylsiloxanes and cold-curing compositions based on them are equivalent in resistance to thermooxidation to compositions based on SKTN low-molecular polydimethylsiloxane rubber (119). For neutralising the HCl which is formed the use of carbonates of barium, calcium or zinc has been recommended (391).

To improve the resistance to thermooxidation, which in turn makes it possible to improve the service life of articles of silicone vulcanisates in air, various antioxidants may be used. The mechanism of action of the antioxidants is bound up with the capacity of polyvalent metals for interacting with organic radicals by changing their valency; this suppresses thermooxidative degradation. However, as yet it has not been possible to get sufficiently accurate experimental confirmation of this mechanism (392). The heat stabilisation depends not only on the nature of the heat stabiliser, but also on its relative amount and specific surface, and the presence of and nature of substrate. For instance, with increase in the specific surface we get an increase in the heat stabilisation effected by ferric oxide (393).

Where there is a substrate the thermooxidative degradation of polyorganylsiloxane vulcanisates is considerably slower (394). In the oxidation in a current of oxygen at 250°C of a rubber film of thickness 0.5 mm, structurised on a quartz substrate, and of a film of thickness 1 mm with no substrate, there were formed in the first case 0.35, and in the second 2.3, cross-links per 100 units of the chain, i.e. there were broken down in these films 6.5 and 15.5 methyl groups respectively (394). The inhibitory effect of the substrate may be explained by the termination of kinetic chains of oxidation on it. A reduction in the rate of thermooxidative breakdown by several decades with the addition of fillers of large specific surface may probably be explained in the same way (394).

The inhibitory effect of such silicates as have a large specific surface is well-known and is much used in cold-curing compositions (395,396).

A considerable effect is achieved by adding 'white black' to silicone elastomers; this raises the initial temperature of breakdown in a current of oxygen by more than 90°C. The inhibitory effect of carbon black is often ascribed to the presence of active groups on its surface (397). The inhibitory action of furnace black, ferric oxide, 'white black' and Aerosil decreases in that order. With the addition of 20 pbm of 'white black' the initial temperature of decomposition of SKTV type rubbers rises by almost 100°C (398). Fine-particle silica, prepared by the plasma method, contains a certain amount of adsorbed or chemically combined water. This water accelerates the hydrolytic breakdown of polyorganylsiloxanes at 130—160°C, this being assisted by the acidic character of the filler. With the addition of Aerosil which is produced by pyrolysis of silicon tetrachloride in a current of oxygen and modified with trimethylsilyl groups, the initial temperature of thermooxidation of silicone elastomers rises by 50°C (116).

On the surface of silicon dioxide there are (sic) residues of the initial sodium silicate, which influence the thermal degradation, and ions of alkali and alkaline earth metals, which bring about breakdown of $\rightarrow$Si—O—Si$\leftarrow$ groups (400). Maximum deactivation of polyorganylsiloxane-α,ω-diols is achieved by the addition of 30 pbm of U-333 'white black' (398). With the use of freshly calcined U-333 the degradation in air is speeded up somewhat (398).

One method of improving the heat resistance of organosilicon rubbers is heat treatment (115).

Particular interest attaches to certain compounds of iron or titanium which are effective stabilisers against thermooxidative degradation. Oxides of titanium or iron are used particularly often for the heat stabilisation of cold-curing organosilicon compositions (401). It has been suggested that at high temperatures polyorganylsiloxanes react with organic salts of iron to form iron siloxanes, which have a heat stabilising effect (402). For instance, with the interaction of PMS-20 polydimethylsiloxane with caproate, valerate or isovalerate of iron at 240 to 280°C there is formed a viscous liquid product which decomposes on further heating (101, 403). This product inhibits thermooxidative degradation. For instance, the rate of oxidation of PMS-100 at 300°C falls to one 260th. Apparently, in the first stage of the process oxidation takes place at the $\rightarrow$Si—C— group with the formation of a silanol group which is an active centre in the reaction with the iron salt. To a certain extent this is confirmed by the fact that the interaction with the iron salt takes place at the temperature of decomposition of polyorganylsiloxanes. Nevertheless it was not found possible to identify the Si—O—Fe group by IR spectroscopy (404). The addition of 0.07 pbm (per what? Transl./Ed.) of iron siloxanolate (sic) gives a high degree of stabilisation (405).

The following heat resistant additives have been patented: aluminium halides (406), kaolin pigments (407), selenium compounds (408), iron salts of carboxylic acids (409) and various other compounds (410).

A siloxane rubber with improved heat resistance in the presence of oxygen may be produced by the addition of nickel chloride, acetate, octoate or oxide, or vanadium oxide (411), alkoxides of iron or chromium (412), acetylacetonates of zinc, chromium, cobalt, magnesium or nickel (413), metal sulphides or metasilicates (414), PM-70 furnace black or inactive fillers (ZnO, Al_2O_3, TiO_2 or diatomite) (415), DNPD (381), salts of tetracyanoquinonemethane (? dimethide) (416), or aromatic inhibitors of oxidation (417).

Other good stabilisers against thermooxidation of organosilicon rubbers are silicon-containing amines and various polymers with conjugated double bonds (418,419).

The inhibitory effect of aromatic groups is possibly due to their forming complexes with free radicals. For this we may use 2,2-di(?bi)phenyleneoxystannane or 2,2-dinaphthyleneoxystannane (391).

With oxidation of aromatic amines there may be formed oligomeric quinoneimines which are effective stabilisers against thermooxidation. The products of oxidation of diphenylamine or PBN (Neozon D) are more effective as stabilisers for siloxane rubbers than the initial amines (395).

The stabilising action of metal acetylacetonates, which depends on the energy of the resulting bonds, increases (sic) as follows:

$$Al > Zn > Co > Cu > Fe > Ti > Zr$$

An improvement in resistance to thermooxidation may be achieved by the addition of 5,12-dibora-6,13-dioxabenzo(2,4)anthracene (420), also of polyorganylheterosiloxanes of the general formula $XO(R_2SiO)MOH$, where $M = Al, B, P, Ti$; $X = H, COCH_3$ (421).

With such compounds as tris(polydimethylsiloxy)aluminium or tris(polydimethylsiloxy)hydroxyquinolinetitanium, and also oligomers containing Al, B, Ti or P, being used as heat stabilisers there is the possibility of their interaction with the end groups of the rubber. Additions of tetrabutoxytitanium, dibutoxytitanium bis(acetylacetonate) or iron acetylacetonate (the molar ratios per structural chain unit $(CH_3)_2SiO$ being 1:64) in the form of a solution in benzene have a heat stabilising effect, rising in the order given above (422). However, the mass losses with the use of these stabilisers differ only slightly. With rise in temperature there is a rise in viscosity of the organosilicon mixes and gelling sets in. This takes place at temperatures lower than that of the onset of degradation. Above 350—400°C degradation predominates over structurisation. The character and rate of degradation, with the formation of H_2, CH_4, C_2H_6 and certain other pyrolysis products, are identical for these stabilisers at these temperatures.

Most of the heat stabilisers mentioned may be used for unfilled organosilicon polymers. However, many of them are effective for compounded rubber mixes as well.

The heat resistance of silicone vulcanisates is determined to a considerable extent by the compounding ingredients.

According to patent data (423) silicone rubbers may be stabilised with oxides, hydroxides or salts of cerium or of other lanthanides — praseodymium, lanthanum, neodymium and samarium — or also with salts of cadmium or sodium (382,423).

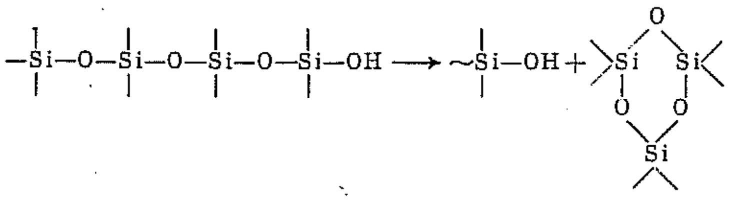
Descriptions have been given of the use, as stabilisers, of cerium tetraiodophthalate (424), of 1,3-diketonates of iron, copper or zirconium or organylsilylferrocenes (425,426), or of derivatives of osmium or ruthenium (427). Additions of 0.02—0.1% of these compounds do not stain the rubbers and are equivalent in heat stabilising to the addition of 5% of iron oxide (428). Complex compounds of certain variable-valency metals, including cerium, raise the resistance of silicone rubbers to thermooxidation by 100—150°C (429).

Successful results are obtained with complex compounds of cerium with disalicyloylpropylenediamine, disalicyloylethylenediamine and acetylacetonate (sic). The mechanism of heat stabilisation with these complexes is based on the fact that with breakdown of the →Si—O—Si← group the cerium complex attaches itself to the anion with the formation of a →Si—O—Cl group. The newly formed complex, containing the →Si—O—Cl group, interacts electrostatically with the corresponding cation, and a →Si—O—Si← group is formed afresh, with the formation of the initial neutral complex.

Salts of zirconium and fluorozirconium acids may also be used as stabilisers (429). We may note the use of polyacrylonitrile (198), and of aromatic amines, e.g. PBN (480). To prevent reaction between the antioxidant and curing agent they are frequently used sorbed on molecular sieves. The use of iron chlorides or of pyrolytically prepared titanium dioxide has been recommended (417). The heat resistance of organosilicon rubbers may be improved by replacing zinc oxide by titanium dioxide (431). It has been suggested that the heat stabilising action of zinc oxide is due to its interaction with benzoyl peroxide in hot curing (432). Nevertheless this action still occurs in cold curing, though such reactions do not occur at room temperature. A mixture of the dioxides of silicon and of titanium has a greater heat stabilising effect than these two oxides used individually (433).

The effectiveness of an antioxidant depends to a significant extent on the method of incorporation. For instance, an antioxidant is 10 or more times more effective when incorporated by chemical combination than by mechanical mixing (434).

Thermal degradation of organosilicon rubbers and vulcanisates has been investigated in an inert atmosphere or in vacuum. The presence of even slight amounts of impurities in the inert gas markedly distorts the picture of degradation. For instance, the presence in argon of at the most 0.02 to 0.03% of oxygen markedly increases the mass loss of the specimen (435). Heating in vacuum at 260—400°C leads to degradation of the macromolecules of polyorganylsiloxanes, with the formation of a mixture of cyclosiloxanes. At the same time there is no noticeable rupture of Si—C bonds (214). With degradation of polydimethylsiloxanes at 400°C there is formed 44% of hexamethylcyclotrisiloxane, 24% of octamethylcyclotetrasiloxane, 9% of decamethylcyclopentasiloxane, 10% of dodecamethylcyclohexasiloxane and 18% of higher cyclosiloxanes (418,436,437). Degradation begins at 220—240°C, while at 350°C almost all siloxane rubbers are degraded completely. Under these conditions there is on the one hand a condensation of the molecules of the polyorganylsiloxanes through reactive hydroxyl end groups, with increase in the MM, and on the other hand degradation of the macrochains, this being the predominant process. Depolymerisation may develop with the participation of hydroxyl end groups as follows:



This scheme (438,439) is confirmed by the formation of hexamethylcyclotrisiloxane with pyrolysis and by the helical structure of the molecules of siloxane rubber, containing three atoms of silicon in each turn (440). With heating to 400°C in vacuum the effective rate constant of depolymerisation is relatively constant up to degree of conversion 50%, after which it falls markedly. With increase in the MM (and, consequently, reduction in the content of hydroxyl end groups) the rate of cleavage of the polysiloxanes decreases.

With the heating of polyorganylsiloxanes or of their vulcanisates in vacuum or in argon there is no detachment of the methyl pendent groups (437). The activation energy in thermodegradation in vacuum does not depend on the MM of the rubber, but, depending on the temperature, is 43 to 178 kJ/mol (12 to 43 kcal/mol). This is less than half the energy of the →Si—O— bond, which is 418 kJ/mol (102 kcal/mol). This lack of agreement may be explained by the fact that the stage which determines the rate of thermodegradation, and which has an activation energy of 166 kJ/mol (40 kcal/mol), is the formation of an intramolecular, cyclic, four-centered transition complex (437). The formation of such a transition state is possible at any point in the siloxane chain and does not require initiation at the chain ends.

Improvement in the heat resistance of organosilicon mixes curing at ordinary temperatures, by the blocking of silanol end groups, is of little use for cold-curing compositions, since in this case we need the presence of other functional groups for the formation of the vulcanisation network. In practice such substituents are incorporated sparsely (341). The blocking of the end groups is effected, for instance, by means of their reactions with monofunctional organosilicon compounds, R_3SiX, where X = Cl,OCOR etc. From thermogravimetric and gas chromatography investigation of the thermal degradation of polyorganylsiloxanes containing trimethylsilyl end groups (MM 8600) or alkoxy groups (MM 11300), the ratio of the cyclosiloxanes in the depolymerisation products is not influenced either by the nature of the end groups or by the MM of the polymer. The products of depolymerisation of these two rubbers at 450°C contain practically identical amounts of hexamethylcyclotrisiloxane (70%), octamethylcyclotetrasiloxane (20%), decamethylcyclopentasiloxane (4%), dodecamethylcyclohexasiloxane (4%) and higher cyclic compounds (1%).

One reason for reduction in the heat resistance of the vulcanisates is the presence of impurities. Even well purified polyorganylsiloxane rubber usually contains 0.05% Ba, 0.01% Pb, 0.005% Al, 0.001% Mg and 0.0005% Ag. Residues of catalysts of acidic or alkaline character sharply raise the rate of thermal degradation (441). Acidic catalysts are as a rule leached out with water. For the neutralisation of alkaline catalysts we use acidic reagents, complexing compounds and so forth.

To remove alkaline agents and to prevent degradation at elevated temperatures there may be added to organosilicon rubbers an ion-exchange resin with active sulphonic groups (442), Hysil X-303 synthetic silicon dioxide (443), alkyl aluminium tetrachloride or phosphonium halides (444), carbon dioxide (445), mono-, di- or trihydric alcohols (446), or oxides of tungsten, yttrium, copper, iron or manganese (389,447,448). Organic tin compounds, which are used extensively as cold-curing catalysts for organosilicon compositions, simultaneously improve the heat resistance of silicone rubbers. The addition of compounds of cerium or other rare earth elements (449) or the incorporation of phenyl groups (378,450) improves the service life under conditions of restricted access of air.

Investigation of the low-temperature resistance of silicone rubbers has become a necessity on account of the increased demand and the lengthening of the service life at low and alternating temperature action (451).

Polydimethylsiloxane rubber has a low glass transition temperature (—123°C). This may be explained by the low molecular interaction and low energy barrier to rotation of the methyl groups (452). For instance, the energy of rotation of the methyl groups in tetramethylsilane is 5.45 kJ (1.3 kcal) at the most, whereas in tetramethylmethane it is 19.0 kJ (4.54 kcal) (453). The homogenity of composition and structure of the globules of polydimethylsiloxane rubbers and their high degree of linearity give them a considerable tendency to crystallisation. The majority of polydimethylsiloxane rubbers and vulcanisates based on them begin to crystallise at a perceptible rate at —25°C, the rate of the process rising as the temperature falls. Polyorganylsiloxanes and their vulcanisates have a high coefficient of crystallisation. With the cooling of a polydimethylsiloxane rubber from —50°C to —60°C the rate of crystallisation rises 30- to 40-fold. From polydimethylsiloxanes of MM 10000, 250000 and 400000 the latter two specimens crystallise at practically identical rates, but the first crystallises more rapidly (311,348).

It is known that polymers never crystallise completely. The degree of crystallinity of polydiorganylsiloxanes amounts to 40 to 50%, while its crystals are small and have many defects (450). Polydimethylsiloxanes differ from the general purpose rubbers. In the vulcanisation of NR, butadiene, PUR and many other rubbers there is formed a vulcanisation network which increases the defectiveness of the crystals formed and reduces the rate of crystallisation. For polyorganylsiloxanes the opposite applies (455). The defective crystals in polyorganylsiloxanes are aggregated with the amorphous regions to form large ordered formations, so-called spherulites. Depending on the conditions of crystallisation, and also on the chemical structure, the regularity of the structure of the polysiloxane chain and the prior thermal action, it is possible for the shape and structure of the spherulites to vary.

The incorporation of phenyl, ethyl, cyanopropyl or certain other groups into polydimethylsiloxanes in place of methyl groups upsets the ordering of the structure and leads to a reduction in the rate of crystallisation. At a phenyl substituent content of 20 to 30 mol.% crystallisation apparently does not take place even at —90°C or below, and the low-temperature resistance of the vulcanisate is determined solely by t_g.

Increasing the number of the modifying units in the macrochain of the rubber retards the rate of crystallisation, but at the same time t_g rises. This must be taken into account in selecting the content of modifying units.

The rise in t_g with the incorporation of a large number of phenyl groups is due not to a loss in elasticity by the organosilicon molecules but to a physical effect of these substituents and consequent reduction in the mobility of the macrochains of the rubber.

With the incorporation of 7 to 10 mol.% of β,γ-(?di)cyanoalkyl groups there is an improvement in the low-temperature resistance of organosilicon rubbers and their vulcanisates. With increase in the number of these groups from 5 to 50% t_g rises from —115 to —90.5°C. Rubbers with a polydimethylsiloxane chain containing 7.8 mol.% of $(CH_3)C_6H_5SiO$ units have the optimum low-temperature resistance (360,451) and t_g —115°C, and do not crystallise at —50°C or even below.

With block distribution of the methylphenylsiloxy groups the crystallisation rate increases by hundreds of times as compared with the statistical distribution. Polymers with block arrangement of $CH_3(C_6H_5)SiO$ units crystallise even in the course of cooling to —78°C. Similarly, vulcanisates based on rubbers with statistical arrangement of the methylphenylsiloxane units crystallise more slowly than vulcanisates of polydimethylsiloxane rubbers.

Polysiloxane (unvulcanised) rubbers crystallise more slowly than their vulcanisates (430,456). For instance, the rates of crystallisation of SKT, SKTV and SKTV-1 rubbers at —20°C and of vulcanisates prepared from them are respectively 0.5 and 1.5, 0.4 and 4.4, 1.1 and 2.3%/h. With lowering of the temperature from —20 to —50°C the strength of these same rubbers increases, while the elongation at break falls. This may be explained by the occurrence of crystallisation, which accelerates particularly with stretching of the specimens. The considerable reduction in the elongation at break in the crystallisation of polysiloxane rubbers clearly distinguishes them from other crystallising polymers, which exhibit only a slight reduction in this characteristic. With cooling of specimens of organosilicon rubbers below —50°C the degree of crystallinity rises, while the tensile strength and elongation at break fall. Moreover, the changes in these two characteristics are not identical at any given temperature, but depend on the supermolecular structure which is formed (457). For a polydimethylsiloxane rubber at —50°C and degree of crystallinity 0.0, 1.7, 3.5 and 5.0 the tensile strength is 5.8, 5.3, 4.5 and 3.7 MPa (58,53,45 and 37 kgf/sq.cm) respectively, while the elongation at break is 235,240,170 and 105%. It has been suggested that at —50°C there are formed sparsely arranged spherulites, which grow larger with time (457).

Electron microscope investigation suggests that large, not interlinked, spherulites, present in the surrounding amorphous material, break up the homogeneity, which leads to a reduction in the strength. With lowering of the temperature of crystallisation and, correspondingly, with fall in the rate of formation of nuclei, there are formed finer spherulites, partially contacting each other. The crystals are found to be more homogeneous, and the strength of the vulcanisates remains at the original level. With further reduction in the temperature of crystallisation there becomes possible the formation of a dendritic (or tree-like) structure. In this case the strength increases.

Where active fillers are used the rate of crystallisation increases at first to a definite limit, and thereafter decreases. The rise in the rate of crystallisation with the addition of an active filler, e.g. Aerosil, may be explained by the action of its particles as nucleus-formers (458). With rise in the filler content there is a reduction in the mobility of the macromolecules of the polyorganylsiloxane rubber, since the particles of filler with large specific surface bring about a straightening and orientation of the segments of the polymer chains as a result of interaction in the polymer + filler system (see section earlier in this chapter, 'Mechanism of the reinforcement of rubbers by fillers'). Nevertheless there are data which indicate that the rate of crystallisation of unvulcanised rubber mixes actually decreases with the addition of a filler (459).

In order to retard crystallisation one may, quite apart from modification of the molecules of the polyorganylsiloxane, turn to the addition of special phenolic inhibitors, which in amounts of 7 to 15 mol.% completely suppress crystallisation.

On the basis of a liquid polydimethylsiloxane containing 8 mol.% of methylphenylsiloxane units there has been developed the cold-cured composition UF-7-21 (460). Let us compare this with one based on the low-molecular rubber SKTN (all the other constituents remaining the same). Under the action of high temperatures (250°C), UV irradiation and service under tropical conditions at 30°C and relative humidity 98% the physicomechanical properties of the two sealing compositions are practically identical, but at minus temperatures the behaviour differs markedly. The SKTN begins to crystallise at —45°C, the highest crystallisation (50%) being at —65°C over a period of 15 min. At the same time SKTNF (?UF-7-21) rubber shows practically no crystallisation over 4 h at —80°C. X-ray investigation confirms its only slight tendency to crystallisation. The onset is evident only with cooling to —80°C for 7 h. Thermomechanical investigation likewise shows a shift of the onset of crystallisation of UF-7-21 into the range of lower temperatures. With lowering of the temperature the tensile strength of vulcanisates based on the Soviet cold-cured compositions U-4-21 and UF-7-21 rises respectively from 1.99 and 2.08 MPa (19.9 and 20.8 kgf/sq.cm) to 18.5 and 20.3 MPa (185 and 203 kgf/sq.cm), while the elongation at break of the two compositions rises only in the range down to —50°C (the temperature of crystallisation of the unmodified sealing composition) (460). With further lowering of the temperature the elongation at break of U-4-21 falls sharply. At —120°C the elongation at break of the composition based on polydimethylsiloxane rubber is practically zero. That based on polydimethylmethylphenylsiloxane rubber has then elongation at break 161%.

ADHESION PROPERTIES

The strength of attachment of organosilicon rubbers to various materials determines their limits of service to a considerable extent (559). The adhesion is determined as the specific work which has to be expended on separating substrate and adherend. The figure for the adhesion depends also on the method of separation — shear along the interface or direct pull perpendicular to the interface. The found figure is usually lower by 2—3 orders than the calculated. The interaction between substrate and adherend is at a maximum if these materials consist of molecules of identical polarity and chemical nature.

Some writers look at adhesion from the aspect of mutual penetration — the diffusion of the macromolecules of the adherend or of its components. As a result of this interdiffusion there is no sharp boundary between substrate and adherend (the rubber Transl./Ed.), while the transition layer which forms in the zone of contact usually has the thickness of a few monomolecular layers. The effect increases with increase in the time of contact.

The surface layers of the material being bonded on or of the underlayer (?adhesive; the terminology appears inconsistent Transl./Ed.) (the primer) penetrate into the recesses and pores of the substrate, which raises the strength of the join. Accordingly for best effect it is better to effect the bonding under pressure, so as to achieve 'hooking joins'. If there are few pores or recesses on the surface, or if the surface layer is compact, then this effect hardly occurs at all. Ordinary glasses, lacquer coatings or polished metals do not form 'hooking joins'. Where there are on the surface a large number of chemically active functional groups (acetoxy, amino, aminoxy (sic), alkoxy or epoxy groups, vinyl groups etc.), which lead to the formation of chemical bonds between adherend and substrate, the adhesion increases noticeably. The adhesion depends also on the thickness of the bonded layer: the thicker it is, the stronger the bonded join (335).

The adhesion of rubbers to a substrate changes with the composition of the adherend + substrate system, and depends on the strength and presence of an undercoat, the standard of preparation of the surface, the rheological properties of the rubber composition, the rate of cure, the temperature, and the rate of peeling (560).

To improve the adhesion of cold- or hot-cured silicone rubbers to various substrates recourse is had to the application of underlayers on the surface of the substrate or of the rubber, or to the addition of special additives to the rubber composition and so forth.

Single-component, or self-vulcanising, cold-cured organosilicon compositions have as a rule good adhesion properties, which cannot be said of two-component compositions. So far no explanation has been found for this.

To improve the adhesion of cold-cured organosilicon rubbers special adherends may be used as underlayers. These underlayers are planned to effect adhesion between a substrate (concrete, ceramics, wood, metal, plastics and so on) and organosilicon sealing compositions. Because of the difference in the properties of the surfaces of the large variety of materials which may be bonded, sealed or 'potted' with a cold-cured composition, it is necessary to select the most suitable underlayer for each case. For silicon rubbers we may use underlayers based on a mixture of tetraethyl silicate and dialkyldiacetoxystannanes (87) with the addition of organylaminoalkoxysilanes or of products of their partial hydrolysis (87); organosilicon resins or cold-cured compositions based on them; products of cocondensation of a polyorganylsiloxane and a resin-type organosilicon polymer; solution of chromium salts in a mixture with a tetraalkyl silicate, boric acid or a trialkyl borate (561); polyisocyanates (562); epoxy resins containing amines as curing agents (562,563); mixtures of polyorganylsiloxanes and silazanes (562); diethoxydiacetoxysilanes (564); alkylaminoalkoxysilanes (565); mixtures based on an organosilicon resin, Portland cement, water and a solvent which has unlimited mixing with water (564); mixtures of esters of orthotitanic acid, a siloxane resin, an alkoxysilane and hydrocarbon solvent; mixtures of fine-particle zinc powder and a product of hydrolysis of an ester of orthosilicic acid and a cold-curing catalyst, etc. (562).

We get adhesion properties also in block copolymers with acetoxy end groups, mixtures of tetraethoxysilane or of products of its incomplete hydrolysis and chelate compounds (566), mixtures of zirconium salts with aminopropyltriethoxysilane, alkoxyisocyanatosilanes (567), products of hydrolysis of tetraalkyl titanates and derivatives of silane with hydrolysable groups (568), polyfunctional chlorosilanes (569), alkenyltriorganylsilanes in conjunction with phosphoric acid (566), the product of reaction of pyromellitic dianhydride and γ-aminopropyltrialkylsilane (570), organosilicon compounds containing alkyl and amino groups, and a mixture of epoxy resin and an amine (459).

There have been recommended (?adhesive) compositions for bonding silicone vulcanisates and a substrate, for instance a mixture of 16 pbm of tetraethoxysilane or of products of its incomplete hydrolysis, 0.75—2.5 pbm of a tetraalkyltitanium, 0.75—5.0 pbm of an alkyltriacetoxysilane and 1 to 20 pbm of a ketone with b.p. 150°C (571). There are also descriptions of bonding mixtures based on diallyl ethers of a bisphenol and a platinum catalyst (206) and polyorganylsiloxanes containing carboxy, amido, nitrile or amino groups (572). Additions of alkoxysilanes and tin compounds may be used (572). There have been proposals for adhesives based on a carboranesiloxane rubber or a mixture of polyorganylsiloxanes with esters of orthotitanic acid (572).

IR spectroscopy has been used to study the interaction of various adhesives, e.g. γ-aminopropyltriethoxysilane, γ-methacryloylpropyltrimethoxysilane, γ-glycidoxypropyltrimethoxysilane and ethyltriethoxysilane with a surface of silicate glass. The hydroxyl groups on the surface of the glass are able to form with these monomers chemical and hydrogen bonds, and there is also possible interaction of silicate glass with the polymer product which forms in the condensation of the initial monomers on its surface.

When cold-cured organosilicon rubbers are used as adherends it is necessary to take into account that the adhesion may be very adversely affected by penetration of water, whether through capillary pores or through the layer of rubber, since the dimensions of the molecules of water are less than the distance between the polycondensation macromolecules (573).

When an organosilicon rubber is being bonded to an organosilicon polymer or to glass the latter is treated with a solution of polyamino-substituted silanes or siloxanes in alcohol, with subsequent hydrolysis and drying of the coating (574). There may also be applied vinyltrimethoxysilane (575) or a mixture of polyesters (?polyethers) and polyamides (576). Before the application of the organosilicon polymer to it the glass fibre is treated with methylchlorosilane vapour (577). The adhesion of silicone rubbers to glass, metals and various polymers may be improved by the use of trialkylsilyl peroxides (578).

In order to improve adhesion the surface of silicone rubbers may be treated with a solution of diaminoxydiacetoxysilane (579) or with the product of hydrolysis of a vinyltrialkoxysilane, with subsequent vulcanisation of the layer applied, which contains vinyl groups, organylsiloxane oligomers with Si—H bonds and a platinum catalyst (579). With the same end in view there may be applied organic salts of metals, e.g. dibutyldilauroyloxystannane (580), esters of orthosilicic acid, or products of their partial hydrolysis (581). Adhesion to polycarbonate is exhibited by organylaminoalkylsilanes (582), tetraethoxysilane in conjunction with powdered zinc, water, and a solvent (583). Adhesion may be increased by adding finely comminuted silicon dioxide (584). Organylaminoalkoxysilanes are adherends to steel, aluminium, copper, nylon and PETP (584). Many more organosilicon adherends are known (492,568).

To improve the adhesion of hot-cured rubber mixes there may be added N,N'-nitroso-N,N'-dimethylterephthalamide, or there may be used, for instance, chemical welding by means of h.f. current (585) or radiation vulcanisation (586).

ELECTRICAL PROPERTIES

Vulcanisates based on organosilicon compositions exhibit good dielectric properties: volume resistivity 10^{13} to 10^{15} ohm cm incl., surface resistivity 10^{13} ohm, tan δ 0.01 to 0.05 incl., and permittivity 3 to 6 incl. They are resistant to corona discharge etc. These properties assure quite extensive use of cold-cured organosilicon compositions for sealing radio, electronic and other electrical articles, where a combination of heat- and water-resistance, elasticity, and good insulating properties are required.

Silicone rubbers not only improve the service life of many articles but are indeed irreplaceable. The dielectric properties of the compositions marketed in the Soviet Union (KL-4, KLT-30, KLF-20) change only slightly with rise in temperature from 20 to 150°C (587). At 20°C $\epsilon = 3.2, 3.8, 3.1$, and at 100°C 2.8, 3.2 and 2.7 respectively, while tan δ remains practically unchanged, and the volume resistivity is, respectively, 10^{14}, 2×10^{14} and 3×10^{14} ohm cm (at 20°C) and 3×10^{13}, 2×10^{13} and 2×10^{12} ohm cm (at 100°C).

These figures may vary somewhat according to the test conditions, the presence of impurities in the compositions themselves, and so forth. Even with prolonged service under tropical conditions the dielectric properties of polysiloxane coatings remain practically unchanged. For instance, after 30 days at 40°C and relative humidity 98% the volume resistivity of the above sealants remains practically unchanged, at 10^{13} —10^{15} ohm cm. The permittivity of silicone rubbers, which are strongly polar dielectrics, changes only slightly as a function of the electrical frequency (588). The changes in the dielectric loss for silicone rubbers in the 0 to 200°C range are likewise very slight. With the addition of Aerosil 300 the dielectric loss rises somewhat (102). The influence of other fillers (mica, copper, titanium dioxide or glass microspheres) has been described (589).

A demand has arisen lately for conductive elastic materials with high heat resistance. With the incorporation of fine-particle conductive fillers the resistance decreases sharply when a particular high filler content is reached. This occurs where the conductive particles form a chain structure (590,591). The effect increases with prior orientation of a ferromagnetic filler in a magnetic field (590).

To produce conductive self-curing adhesive compositions it is possible to add about 80% (?bm) of fine-particle powders of iron, nickel, silver, copper or graphite (592). The marked raising of the electrical conductivity with filler content upwards of 40 pbm is explained by the particles of metal in this case being separated from each other by a distance less than the diameter of the particles themselves, and the incorporation of even relatively small amounts of conductive powders causing a big increase in the conductivity.

Conductive compositions may also be prepared by adding carbon black or by heating the rubber mix to the temperature of pyrolysis of the constituents, which form thermal degradation products exhibiting electrical conductivity (592). The desired result may be achieved by adding polymers of a special type, e.g. containing long chain segments with conjugated bonds or having suitable graft molecules of the 7,7,8,8-tetracyanoquinonemethane (sic) type. By the addition of the last-named compound it is possible to increase the conductivity by 1000 or more times.

SOME OTHER PROPERTIES

Vulcanisates based on cold-curing organosilicon rubbers are characterised by such properties as petrol- and oil-resistance, reduced flammability, translucence, low thermal conductivity, low shrinkage, abrasion resistance, deformation resistance, capacity for taking colours, fungus resistance, and so forth. Certain of these properties are generally inherent in materials based on polydiorganylsiloxanes, while others may be conferred by modifying additives or by varying the structure of the polymer. For instance, organosilicon materials do not incline to colour, but they acquire a desired colour by various measures.

Fire resistance. Silicone rubbers and vulcanisates based on them have low combustibility compared with the majority of general purpose rubbers. Under the action of an open flame they burn, oxidising to form silicon dioxide. The surface skin thus formed hinders penetration of the flame into the body of the material. We find somewhat higher fire resistance in polyorganylsiloxanes which contain phenyl groups attached to the silicon atoms (593). Some organosilicon vulcanisates prepared using special fire-resistant additives, withstand the action of a flame at above 840°C for several minutes, extinguishing within 10—15 sec after the action of the fire stops.

Articles of silicone rubber which do not catch fire until at least 60 to 70 sec action of an open flame have been publicised (594). The room temperature curing fire-resistant silicone rubber Sylgard-170A is recommended for potting, encapsulation and coating in electrical and electrode equipment (583).

Fire-resistance may be improved by adding platinum compounds to an organosilicon composition (595).

In preparing fire-resistant organosilicon compositions there may be used a number of polymeric compounds of silicon containing phosphorus atoms either in the main chain or in pendent groups (572). Phosphoric acid esters may be incorporated as fire retardants. A similar result is obtained by adding such chlorine-containing compounds as chlorinated paraffin wax, tetrachlorophthalic anhydride, tetrachlorobisphenol A, a chlorinated diphenyl or a mixture of these compounds (596,597). Fire-protective properties are exhibited by antimony chlorides or the products of their hydrolysis or alcoholysis (597,598), by oxides or halides of arsenic (597), by sodium bicarbonate (599), or by silicon carbide in conjunction with a high m.p. fibre (488). Self-extinguishing properties are typical of polyorganylsiloxanes with halogenated radicals (595,600), or of polyorganylsiloxanes in conjunction with channel black and platinum compounds (595) or with platinum applied to carbon (601).

A non-flammable cellular silicone vulcanisate may be obtained by adding nickel bromide, pentabromoethylbenzene or pentabromotoluene (601,602). The incorporation of one atom of chlorine into each phenyl group in a polymethylphenylsiloxane increases the fire-resistance 1.5-fold; adding two atoms doubles the fire-resistance (598).

Compression set. One important feature of cold-cured vulcanisates is their resistance to set. The extent of set is affected by the structure of the rubber molecules, and the nature of the vulcanising agent, fillers and curing catalyst. With hot-curing mixes the compression set can be reduced by incorporating 0.1 to 0.5% of methylvinylsiloxane units. At the same time we maintain the heat resistance and elongation at break (602). This also makes it possible to reduce the amount of peroxide needed for the curing (e.g. benzoyl peroxide) from 1.5—3.0 to 0.5—0.75% bm, the number of resulting crosslinks being determined mainly by the number of methylvinylsiloxane units added and depending to a lesser extent on the concentration of peroxide initiator.

The compression set of cold-curing organosilicon vulcanisates depends on the type of catalyst and the crosslinking agent. A widely used curing catalyst such as stannous octoate gives a better result than dibutyldilauroyloxystannane. Inert fillers also have a good influence. Raising the content of compounds of acidic or, particularly, basic character increases the compression set. This undesirable result occurs in the presence of as little as 0.03% of KOH. A mixture of cadmium silicate and nickel oxide may be added to improve the resistance to compression (603).

Thermal conductivity. The thermal conductivity of organosilicon vulcanisates (10^{-3} W/m K) is twice that of organic vulcanisates. It depends little on the type of silicone rubber, and it decreases with rise in the temperature of service of the articles. This may be explained (604) by increase in the distances between the molecule chains of the elastomers. With rise in the amount of filler (up to 15% bm) the thermal conductivity increases almost linearly. The Soviet sealant VGO-3 exhibits relatively high thermal conductivity. For organosilicon mixes used in fluorescent lighting zinc oxides or zinc chalcogens may be used as fillers (605). In order to improve thermal conductivity metals and their oxides (606) or microspheres of beryllium oxide may be added to organosilicon compositions (607). The thermal conductivity is influenced also by the type of carbon black (608).

Abrasion resistance. The abrasion resistance of vulcanisates may be improved by the use of graphite of particle size 0.01—0.001 mm (609), or of fine-particle hydrated silicon dioxide treated with a complex prepared from chromium oxide or zirconium oxide by means of a carboxylic acid (610).

Resistance to fungi. Organosilicon rubbers and materials based on them have higher resistance to fungi than butyl rubber, NR, SKI-3, SKD, SKMS-30, SKEP and many others (611,612). In tropical service at 28—35°C and relative humidity 98% rubber articles are covered with mould with the passage of time. The conditions are particularly favourable to this development in sites with limited access of air, or in direct contact with water or soil, or with a medium containing carbon dioxide and nitrogen. Mould adversely affects the optical and anticorrosion properties of organosilicon materials or coatings, causes loss of seal, and reduces the surface resistivity. Compounds containing mercury or antimony may be added to improve resistance to fungi.

Water resistance. Silicone rubbers exhibit low water absorption, not above 1% even after the specimen has been in water at high temperature. The water molecules which have penetrated into the interior occupy the cavities between the clumps of the siloxane macromolecules (613).

The water absorption of the fillers has a considerable influence on the thermomechanical properties of the silicone vulcanisates. Fine-particle powders absorb water to differing extents depending on their chemical nature, specific surface and methods of preparation. The water absorption of 'white black' (silica filler Transl.) is 6.5%, that of powdered quartz 0.25%, that of zinc oxide 3.58%, that of iron oxide 1.13% (604,614), and 'white black' improves the water resistance of the vulcanisates. Modified Aerosil reduces the atmospheric water absorption and improves (sic) the vapour permeability (614,617).

Service properties. Vulcanisates of low-molecular organosilicon rubbers are in effect elastogens, since they acquire elastic properties only after curing, but until then are pseudoliquids (616). They are very resistant to UV irradiation, oxygen and ozone, and can be used at 160—180°C for several years, while they are exceptionally weather resistant. The gas permeability of silicone vulcanisates is 10 to 20 times that of ordinary vulcanisates. Materials based on silicone vulcanisates remain elastic after the action of a radiation dose 1.2×10^5 to 1.2×10^6 C/kg (5×10^8 to 5×10^9 roentgens). Dimethyldiphenylsiloxane rubbers exhibit higher resistance to radiation than polymethylphenylsiloxane for equivalent molar content of phenyl groups. One valuable property of silicone vulcanisates is their resistance to contamination (622). Organosilicon materials take the colouring agents used commercially only poorly. To improve this there may be added to the vulcanisates resins which are compatible with the silicone rubber, e.g. polymerised rosin (623).

Tear resistance. To a considerable extent the energy of tearing is dissipated irreversibly with growth of the tear apex. In the case of non-crystallising rubbers it depends on the crosslink density (expressed as $\frac{1}{2}M_c$, where M_c is the number-average MM of the chain segments between the crosslinks of the polyorganylsiloxane) and the type, amount and particle fineness of the filler. For hot-cured organosilicon vulcanisates the tear resistance rises linearly with reduction in the crosslink density. For instance, reduction in the crosslink density by 39% raises the tear resistance at room temperature by 76%. It is, however, necessary to take into account that any considerable reduction in the crosslink density may sharply reduce the elasticity and increase compression set.

The tear resistance increases with rise in the degree of filling and with reduction in the particle size of the filler. This means that interaction between the filler particles and the rubber molecules does not lead to the formation of distinctive crosslinks. With increase in the specific surface of the filler and improvement in its wettability by the polymer there is a rise not only in the tear resistance but also in the tensile strength, elongation at break and modulus of silicone vulcanisates. The tear resistance is practically independent of the nature of the substituents attached to the silicon atom. Silicone rubbers with relatively high tear resistance have been produced recently. Whereas standard vulcanisates of organosilicon rubbers which cure at room temperature have a tear resistance of 8 kN/m (8 kgf/cm), those with the improved tear resistance achieve 20 kN/m (20 kgf/cm) (614). The latter vulcanisates have 'knotty' tear — with the application of force they rupture (or tear) in the direction of the force which is applied (sic). The tear resistance increases with the addition of finely comminuted PTFE (617).

Resistance to solvents. The serviceability of the vulcanisates in solvents depends largely on the chemical nature of the solvents. The durability is determined first and foremost by the interaction of the surface layer of the polymer and the liquid.

To improve the resistance of vulcanisates to the action of benzine, oils and aliphatic, aromatic or chlorinated solvents, dimethylsiloxane rubbers may be modified by replacing some of the methyl groups attached to the silicon atom by trifluoropropyl or cyanoalkyl groups (187,618). We find the lowest swelling in these solvents where the vulcanisates contain only methyltrifluoropropyl or methylcyanoalkylsiloxane units.

Cold-cured vulcanisates of this type are practically not inferior in swelling behaviour to hot-cured. A vulcanisate of SKTFT-100 rubber has, after holding in T-1 fuel for 72 h at 200°C, swelling by 7.5% at the most, tensile strength 4.2 MPa (42 kgf/sq.cm) and elongation at break 565%. With rise in the content of cyanoalkyl units from 20 to 50% the swelling in isooctane at 50°C decreases 5- to 6-fold, that in T-1 at 200°C 2- to 3-fold, and that in hypoid oil at 130°C 2.5- to 3-fold (619). The degree of swelling in solvents where the organosilicon vulcanisates contain equal numbers of cyanoethyl or cyanopropyl units is practically equal. The oil resistance and resistance to solvents is higher for polydimethylsiloxane vulcanisates than for polymethylphenylsiloxane (620).

To reduce the swelling zinc borate may be added to the vulcanisates (504), or they may be given irradiation in addition. The addition of finely comminuted metallic silicon likewise improves the oil resistance (621).

CHAPTER 4

USES OF COLD-CURING ORGANOSILICON COMPOSITIONS

BUILDING

Liquid organosilicon monomers and polymers and materials based on them are widely used for water-proofing building materials and structures (624—626). Particularly valuable features are their high water-repellence, light-, ozone- and weather-resistance, their resistance to mould fungi, non-toxicity, good (sic) vapour- and gas-permeability, and stability to low or high temperatures and to sudden temperature differentials. The waterproof organosilicon coatings used in building have also a number of specific 'building' properties: they preserve the colour and texture of the surface, and they penetrate into the pores of the material and bind firmly to it. No less interesting to the builder are silicone resins, unvulcanised rubbers and cold-curing rubbers.

In present-day building, particularly in multi-storey buildings, we need reliable joining of metal structures with the building stone, brick, concrete, asbestos, glass fabric or ceramics, and also sealing of joins and interlayers (627,628). Frequently we need for joining structures flexible sealing materials with differing thermal expansions (sic) (629).

Organosilicon cements for building exhibit good service life and good adhesion, and require less labour. The place of drying-out sealants based on vegetable oils and alkyd resins is being taken by new materials, in particular organosilicon sealants, especially in high buildings, underground structures, and also under the conditions of the Far North.

The use of silicone vulcanisates is most profitable, since it makes it possible in general to increase the useful life of structures and to reduce running costs (630). The weathering resistance of silicone vulcanisates and their resistance to UV radiation have been demonstrated by long-term full-scale tests over 15 years, and also by accelerated ageing equivalent to service over 30 years (627). These tests revealed no significant deterioration in the properties of the vulcanisates.

The materials used in building are black, white, red or silvery. They do not leave any stain on the building materials. The good adhesion to metals and many building materials (concrete, brick, etc.), durability, capacity for taking colours, and other properties have made it possible to use cold-curing organosilicon compositions with success in buildings (587). The higher cost of these materials, for instance as compared with thiokol sealants, is more than compensated for by the long service life.

Silicone elastomers curing at ordinary temperatures were used in the building industry only comparatively recently, at the beginning of the 1960s. The volume of production of silicone elastomers for use in building is continuing to increase (631,632).

In the U.S.A. silicone sealants make up 15% of all the sealants used in building (1250 t). In the Soviet Union the first trials of these materials in building were in the middle 1960s.

The expenditure on running repairs of tanks and reservoirs has been considerably reduced by sealing these with solid, flexible and water-impermeable vulcanisates based on silicone sealants (633). After 5 years service the silicone sealants still remain firmly attached and flexible, in spite of the constant moisture and high temperatures. It is no longer necessary to reseal baths and showers once or twice a year (629,633).

Single-component silicone sealants may be used to seal the expansion joins between the edges of ceramic decorative tiles (634). They allow repeated expansion and contraction of building structures without resealing and exhibit good resistance to cracking and loss of strength.

Silicone sealants are used in making landing and take-off strips, for bridges, for filling expansion joins in roadmaking, for plugging brick facing, for sealing tiled floors and tiled walls, for ducting, for ventilators, for sealing vacuum and sanitary equipment and heavy structures and apparatus used in the chemical industry, particularly where sharp fluctuations in temperature occur in service (634), and also for insulating heating elements (635).

Cold-curing organosilicon sealants may be used in making stained glass panels (636). These panels are light and resistant to weathering, they are decorative in transmitted and reflected light, and they have good heat and sound insulating properties. To increase rigidity the panels may be combined with sheet glass or other materials.

The sealing and covering of roofs of especially complex configuration or with steep slope is exceptionally difficult and in a number of instances practically impossible. It has, however, been found possible to use cold-curing compositions for this purpose (627). The roofs may be made of plywood, concrete, iron or other structural material. To secure the composition better to the roofing surface this is covered with an adhesive underlayer or primer, and then the composition is applied with a brush or roller. It is necessary to cover sites of possible accumulation of water with particular care.

Their good waterproofing and resistance to chlorinated water make it possible to use silicone materials to make pools and aquariums. These sealants have a number of advantages over thiokol, polyisobutylene and certain other types. They are, for instance, stronger than the thiokol types; the tensile strength is 0.8 to 0.9 MPa (8 to 9 kgf/sq.cm) and 0.2 to 0.3 MPa (2 to 3 kgf/sq.cm) respectively (637,638).

The extensive possibilities of using silicone sealants in building may be illustrated by a few examples.

The Soviet sealant Viksint U-1-18 has been used for surface sealing of large-panel buildings. This two-component sealant may be applied with a spatula, or, after dilution with benzine, with a brush. The amount used is 0.225 kg per metre of joint, or 450 kg for an 80-apartment dwelling block (overall length of joints 2000 metres). The width and thickness of the joint are 10 and 2 to 3 mm respectively. The selection of the amount of catalyst and a number of other factors make it possible to use this sealant at from 5 to 30°C. To optimise the composition many fillers may be used — whiting, ground sand, cement, talc, asbestos, or aluminium powder (639).

The single-component cold-curing sealant Silastic 733, based on a fluorosilicon rubber, is used as a sealing material in reservoirs for storage of fuel, solvents or many other chemical reagents (588).

The cost of periodic sealing of buildings and the equipment in them in the South Illinois State University was considerably reduced by using a cold-curing silicone rubber as a putty. This material was used for sealing of 300 buildings on the university campus...it makes joints water-repellent and weather-proof (633).

In one building of a factory using atomic energy, built up from 750 reinforced concrete panels, the joints of the panels were sealed with Dow Corning Silastic 780, of the colour of natural stone. A silicone sealant is also used in the joins between the horizontal (?) wall panels and the composite pillars, covering the vertical load-bearing parts of the reactor housing, and also in the joins of metal roofs and exhaust openings.

Silicone sealants, such as Silastic 780, have been used to seal an extremely large dome of aluminium, of height 21.3 m and surface area 4700 sq.m. The dome is mounted on 1300 anodised aluminium panels fitted together. The colour of the sealant is similar to that of gold. The total length of the sealing join is 4572 m (633).

AVIATION AND SPACE TECHNOLOGY

The materials have to withstand great alternations of thermal stress within very short time intervals. The requirements are rising constantly.

Silicone sealants and compositions have been adopted extensively of late in aviation (222). In one large passenger plane there are used upwards of 20 kg of sealants based on organic or organosilicon rubbers.

To prevent leakage of fuel (including that based on hydrogen peroxide), oil and water, aircraft and spacecraft engines, in particular components which are under pressure (e.g. pumps and ducting) are frequently sealed with siloxane, and particularly fluorosiloxane, sealants. These do not lose their properties with service, and they withstand considerable temperature and vibration loading. They are particularly convenient for maintenance and repair work. In cases of damage these coatings prevent loss of pressure-tightness of the equipment (640).

The following requirements are posed for silicone adhesives: they need to have good adhesion and to retain flexibility in the temperature range —40 to 70°C. They may be used to attach nylon fabric coated with organosilicon rubbers to aluminium, or moulded nylon articles, or moulded nylon to aluminium. Silicone adhesive-sealants meet these requirements fully (633).

Cold-curing compositions are used for attachment of the parts of the inflator system for rescue chutes (641), in the pressure system for opening emergency exits (642), in fire-protection equipment, and for making helicopter nose cones and the moulds for these (643).

They are used also in laminated splinter-proof glass (644), for preventing leakage of oil in ducts, motors and pumps (645), for fireproof partitions, and for heat insulation for fuel tanks. Silicone compositions can be applied through a nozzle by means of hot air, and are converted into a vulcanisate within 5 min at 150°C. These vulcanisates do not catch fire even under the action of a gas flame at 1000°C over 30 sec. High fire-resistance is, of course, achieved by the use of fire-retardants. An insulating crust forms on the surface of the material within 60 sec at 2760°C (646). There are indications of short-term resistance of organosilicon rubbers even at 5000°C. Heat-resistant inks based on polyorganosiloxanes are used for marking metals in aircraft construction.

In addition to their capacity for service over a wide range of temperatures, from —60 or even —100 up to 300—350°C silicone vulcanisates stand up to extreme loadings for short periods, and go on insulating the parts for a short time even after breakdown.

Silicone coatings prepared by vulcanisation are used in military and space rockets, to insulate metals from the action of heat, moisture and other factors. In space rockets, e.g. Gemini, there are used ablation coatings weighing 50% less than previous examples (638). Silicone compositions are used in rocket technology for sealing built-in fuel compartments which are used in a medium of (sic) rocket fuel (nitrogen tetroxide etc.).

Organosilicon compositions which cure in 10 to 35 min and are supplied as liquids or pastes may be applied to metals, plastics or ceramics by dipping, pouring on, spraying or spreading (639). Under the action of high temperatures the material swells up, which increases its effectiveness as an ablation-type protective coating (684).

For employment in space craft modern synthetic materials have to satisfy two requirements above all others: they must not give off noxious, or poisonous, gases under high vacuum conditions, and they must not ignite in an atmosphere of pure oxygen. Of the large number of materials tested in this connection, such as epoxy resins, PUR rubbers, polycarbonates and silicones, it is only the last-named which meet the requirements (685). For instance, the loss in mass in vacuum (at residual pressure 1 × 10^{-6} mm) in 24 h at 220°C is less than 7% (686).

Adhesion-type seals are used as a joining material between the collar of a space suit and the helmet made of polycarbonate, as a lining in a space suit, for sealing headphones for simultaneous translation and telephone leads (687). They are used also in special motors in space rockets for sealing and protection of a variety of equipment (635).

Sealants based on silicone rubbers are used in many parts of space travel equipment. They are used to protect the launching pads and the inlets and outlets of leads. To secure ablation material we use an adhesion-type underlayer, Primer 1200. Without an ablation coating the equipment breaks down, since at the launching of the rocket the temperature reaches 2600°C, and the velocity of the gas around 180 km/h. An envelope of Dow Corning 93—072 silicone rubber is used to secure the insulation to the outer casing of the rocket motor, protecting it from the direct impingement of flame in the event of fire (633). If the insulation breaks down a temperature of 2600°C acts on the casing of the motor, causing its breakdown.

Coatings of silicone rubber have a number of advantages over other materials, since they are less subject to residual deformation at high temperatures and pressures than other materials. Silicone coatings do not require the use of parting agents.

The following are some examples of the use of silicone sealants in aviation and space travel technology.

Organosilicon sealants are used in the equipment of the X-15 plane.

Silicone and fluorosilicone sealants are proposed for extensive use in 'Concorde' (684). These materials were selected for their flexibility at high and low temperatures and their resistance to oils, solvents and fuels. Annular seals in fuel ducting are made from a fluorosilicone rubber. They are used also in pumps, distributor valves, measuring instruments and electrical connections, since they have good service properties. Silastic 731 and 732 are used to secure seals of RTV silicone rubber to the folds of a service hatch and for the sealing of the fuselage which is required for high-altitude flying. Silastic 2551 is used to seal a device for testing the doors of the inspection port of the engine.

In the instrument for controlling the angle of longitudinal motion and the angle of banking of a satellite an encapsulator of cold-curing silicone rubber maintains identical temperature on the objective and inside the jacket of the objective, without allowing leakage of gas. The lenses of the objective are constantly within the space zone and are subject to direct radiation. To ensure receiving correct information the objective has to be at a temperature as near as possible to that of the aluminium envelope (633). As intermediary material to conduct the heat Dow Corning 93—500 sealant is used. Under space conditions this sealant effectively prevents leakage of gas and retains its physical and chemical properties in the temperature range —65 to 200°C. Camera and other brittle instruments on board the Apollo spacecraft are fitted for maximum protection on special underlayers of Microsil (sic) organosilicon rubber. This material has low flammability, low compression set under loading, and is resistant to extreme temperatures (12,635).

In the first stage of the Polaris rocket 50 kg of organosilicon elastomers are used in protective coatings.

An adhesion-type sealant based on silicone rubber is used to fasten parallel rows of copper tubes used as heat conduits between electronic components and the heat dissipation system in the Apollo spacecraft (633). They are used for sealing the power units, to avoid leakage of fuel and oxidants. These same materials may be used to seal the aluminium tubes joining sections of a rocket, some rivetted joins, and projections of power units.

In the launching silo of the Titan-11 intercontinental ballistic rocket high temperatures and high-velocity gas currents are created. At the U.S.A. military air base at Vanderberg (California) the equipment in the launching silo is protected with a silicone ablation coating of thickness 6 mm. After the launch of a rocket the part of the silicone coating which has been heated up is removed and replaced by new. Within a few weeks of a launch the silo can be used for another rocket. Previously two to three months had been required for the restoration.

RTV-630 sealant, which has good physicomechanical properties (tensile strength 6MPa (60 kgf/sq.cm) and elongation at break 300%), has been used for soles, tips for glove fingers, overshoes and suits for the astronauts on board the Apollo spacecraft (687).

MOTOR TRANSPORT

The motor industry is a relatively new but promising user of RTV silicone compositions (647). Chloroprene gaskets in motor engines have now been supplanted by single- or two-component silicone sealants. They are very convenient, being used actually on site. They are sometimes used to fill cavities appropriately, giving a lining e.g. for a valve housing. Silicone rubber may be used to seal the front of a car and the engine, sumps, and joins of tubes for fuel and lubricants. Sealants may be used in silencers and for lining the body and parts of the engine. Single-component sealants are supplied for greater convenience in tubes, and can be in various colours, or colourless. They are easily secured to any part of the body or to the surface of the engine; they are resistant to water, lubricants and weather, they do not shrink, crack, or fracture, and they withstand temperatures from —73 to 232°C (647). The sealants used in the motor industry cure at ordinary temperatures within a few minutes of being poured.

One valuable property of silicone materials is their capacity for taking any desired shape, making it unnecessary to buff the surface. Silicone sealants give prolonged continuous service in protecting crankshafts. They may be used in plate-type flap valves and sockets for sparking plugs.

Seals shaped on site may be used to seal the crankshaft housings of two-stroke engines. Housings made of an aluminium casting consist of two parts attached together. Although the surfaces are closely adjusted, slight leakages of oil are still possible and may seriously affect the service properties of the engine. The crankshaft housing must be absolutely pressure tight. To achieve this adhesive sealants are used. These materials have the necessary consistency, they are easily applied, they do not give off toxic products on curing, they cure relatively quickly, and remain elastic throughout the entire service life of the engine (633). Engines for racing cars can be used within an hour of the application of the sealant. Adhesive sealants are used also for sealing windows, car door frames, and in measuring devices and other units which are subject to water leakage.

Wind screens may be secured strongly by means of self-curing sealants. Their vulcanisation takes place in as little as 15 min after the application of the sealant to the surface (or, rather, the mix gels and loses its flow) and a strong film of the desired colour is formed (633).

In the running of high-speed cars the temperature in the gear box reaches 176°C, and in some parts of the engine 315°C. Accordingly approximately two-thirds of all the boots for the sparking plugs are made of heat-resistant silicone rubber. Seals of this rubber withstand the severe vibration set up in the running of the car, and remain serviceable for 60000 to 80000 km. Metal and paper gaskets do not stand up to such conditions. Leakage of oil and water into the engines of racing cars naturally means a loss of performance. In these engines the temperature reaches 120°C and the oil pressure up to 0.85 MPa (8.5 kgf/sq.cm); in addition, considerable roughness results. At the high speeds of racing cars water getting into the oil system converts the oil into an emulsion, which may ruin a costly engine within 5 min. To solve this problem a special silicone sealant has been developed, which protects particularly dangerous zones in the engine and prevents leakage of oil from the engine or the penetration of oil into the crankshaft housing. Silicone gaskets in engines of racing cars, of power ranging from 367.8 to 615.2 kW, have been used in the U.S.A. since 1966.

The cost of the gaskets used in a single car is one dollar, which, in view of the great volume of production of motor vehicles, shows the evident good prospects for their use.

ELECTRICAL AND RADIO INDUSTRY

Organosilicon compositions and sealants are used particularly widely for impregnation, encapsulating materials and sealing coatings in present-day electronic and radio articles (648,649). The total volume of the organosilicon mixes used in these industries is relatively low, but their importance cannot be doubted. The standard properties of silicones are exploited: their excellent weathering resistance, their resistance to visible and UV light, their ozone and moisture resistance, their exceptionally slow thermal and electrical ageing, their inertness to many chemical reagents, and their good adhesion.

The requirements for insulation in the ... industries are determined to a considerable extent by the conditions of service and the service life. Articles based on organosilicon rubbers which remain serviceable at 180°C for 25,000 hours have made it possible to establish a new class of resistance to heating for adoption in the U.S.S.R., class N (102). Not only the heat resistance of the vulcanisates based on silicone mixes, but also the only slight variation in the electrical characteristics within the working range of temperatures, are exceptionally valuable.

Single- and two-component RTV organosilicon compositions may be used as various types of electrical insulation (337), as moulds for semi-conductor instruments (635), as seals for electrical input connections, in distributor boxes (651), for encapsulating cable joints, for condensors, resistors, transformers, and electric and radio circuits (652), for coating porcelain insulators (653), for potting, for damping, monitoring and measuring equipment on rocket test beds (654), and for sealing up ferrite elements in electronic and computer apparatus (655).

Silicone insulators are considerably lighter than procelain, and do not form cracks which give rise to possible leakage and short-circuiting (656). Fluorosilicone sealants have insulation resistance upwards of 10^{10} ohm (sic) even under arduous service conditions (70°C, 100% humidity) over 18 months (657). Conductive rubbers may be attached by means of electrically conductive two-component seals filled with powdered nickel (658). These materials may be used to secure instruments to a chassis (633). The white bonding agent-cum-sealant RTV-738 may be used to seal electronic equipment which is subject to corrosion, and in domestic utensils (633).

Organosilicon compositions may be used to seal cables. It is possible to prevent defects caused by corrosion under weathering, by using organosilicon sealants which protect them from the penetration of water and salts from the soil (633).

The materials used in semi-conductor instruments must give reliable protection of their surfaces, possess good thermomechanical, dielectric and adhesion properties, and also prevent the migration of ions to the surface. These requirements are met by oil- and petrol-resistant compositions based on the Soviet fluorosilicon polymer SKTFT-50. The paste-type and fluid sealants 14-S-1 and 14-S-2 exhibit, even without using an underlayer, satisfactory adhesion to steel, aluminium, titanium, and organic and silicate glasses. These sealants may be used for sealing strain gauges and electric and radio measuring equipment (659). Organosilicon compositions and sealants may be used to protect leads of small cross-section projecting from sealing collars. After the composition has hardened the system functions well (660). Electrodes may be made by suspending spectrally pure graphite in an organopolysiloxane, followed by cold curing (661).

General Electric are producing transparent coatings for electric bulbs. Such a coating transmits more than 95% of the light flux and prevents splinters flying off in breakage; it withstands the action of ice, snow, rain, lightning etc. It combines well with shellac, nitrocellulose or chlorinated PVC coatings (662). The Soviet composition KLT-50 attaches satisfactorily to glass, enamel or silicate coatings, and to the porcelain parts of electric instruments. When K-100 underlayer is used the adhesion to steel, aluminium, copper, bronze, titanium, chromium, nickel, tin, lead, organic glass (presumably PMMA Transl.), Kapron, graphite and other structural materials is perceptibly improved. The two-component potting composition KLSE is used with good results for insulating the soldered joins of windings, rotors and stators, and electric generators and the housings of electrical machinery. It is used also for potting the stator windings of A-81-4 electric motors which are used for oil pressure pumps. This composition has been used with good results to replace traditional materials such as mica. It is easier to fabricate, it reduces the temperature differential in insulation, and it has good mechanical and dielectric properties.

Many of the sealing materials used extensively in Soviet industry, e.g. epoxy resins, crack under the influence of mechanical and temperature effects. In this respect elastic vulcanisates obtained by cold-curing of organosilicon compositions are more reliable. The Soviet compositions KL-4 and KLT-30, and the sealants Viksint, PK-68 and VGO-1 are used to protect magnetic circuits and iron-nickel alloys. KL-4 is recommended as a damping material for protecting toroidal Permalloy cores. The single-component KLT-30 is used in making lamp control panels. VGO-1 has been used for sealing laminated Permalloy cores in l.f. transformers.

For sealing radio articles operating in high humidity and at temperatures from —60 to 300°C it is possible to use silicone compositions curing at ordinary temperatures: Viksints K-8, U-1-18, U-2-18 and U-4-21, VGO-1 sealants, and the compositions VPG-2L and Silpen, which with vulcanisation form a sponge rubber. These have good flow, which makes it possible to fill small orifices and recesses.

KLT-30 with K-100 underlayer is used in the high-voltage thyristors T-320 and T-500, as a protective structural material, which locates the thermal compensation plates with the rectifying elements when these are assembled in the housing.

The foam-type sealant VPG-2L, which cures at room temperature under the action of atmospheric moisture, has a foaming ratio of 1.8 to 2.0. The vulcanised materials have good electrical characteristics, and do not corrode copper. Their pot life, i.e. the time up to the mix losing fluidity, is 20 min. Single-component mixes of certain types have good adhesion, which makes it possible to use them in the electronics and radio industry as bonding agents + sealants. For instance, the Soviet Elastosil, which has good adhesion to various materials, may be used to seal electronic equipment, and also in repairing articles which have been sealed with other silicone materials.

MEDICINE

Thanks to their combination of useful properties (non-toxicity, biological inertness, water repellence, adequate resistance to the action of acids or of fungicides, their lack of odour, their low flammability etc.), silicone polymers which cure in the temperature range 20—40°C (i.e. even at the temperature of the human body), may be used in medicine. It is useful to divide the cold-curing compositions used in medicine into two groups: (1) those used directly within the human organism, and (2) auxiliary materials.

The human organism resists invasion by a foreign body. Rejection reactions occur, and tumours are formed, etc. Accordingly strict requirements are laid down for materials to be introduced into the organism.

To prepare the organosilicon vulcanisates used in medicine we employ polyorganylsiloxane elastomers, silicon dioxide and a curing agent. No other compounding ingredients (heat stabilisers, colouring agents, vulcanisation inhibitors etc.) are used because of the danger of unfavourable action on the organism. As a rule, the curing catalyst for two-component sealants for medical use is stannous octoate. By itself this causes reddening of the skin and eye irritation. Nevertheless a medical grade vulcanisate introduced into tissue, like a silicone rubber by itself (of course, not containing any impurities harmful to the human organism) has no influence on the skin (664). A silicone rubber produced at ordinary temperature using such a common catalyst as dibutyldilauroyloxystannane has an adverse effect on the skin and accordingly cannot be used in medicine.

Silicone rubber is the most common material for implantation in human organs, ranging from finger joints to parts for an artificial heart. With polyarthritis sufferers success has been achieved in the use or artificial finger joints of silicone rubbers. There are plans for the production of artificial joints and bones for use in orthopaedics and plastic surgery (665). It is intended to produce for implantation small wrist bones, fore-arm bones, elbow joints, and heads of bones. Prostheses have been devised for replacing the joints of the thumbs and great toes. Articles of silicone rubber are softer than bone and do not damage the tissue. Silicone prostheses have a smooth surface, and they restore and maintain the motor functions of the extremities, and retain good cosmetic appearance. Since it is biologically and mechanically harmless, the prosthesis is surrounded by a capsule of supporting fibres, which maintain the stability of the joint + tissue system (633). Silicone materials are being used extensively in surgical operations on the facial part of the skull (ear, nose, chin and jaw), and in urology.

Membranes based on organosilicon rubbers are used to saturate the blood with oxygen. With membrane thickness 0.02 mm their gas-permeability to oxygen is 15.68×10^{-6} m $\times$ day^{-1} $\times$ Pa^{-1} (1568 l $\times$ day^{-1} $\times$ m^{-2} $\times$ atm^{-1}), and to carbon dioxide 83.04×10^{-6} m $\times$ day^{-1} $\times$ Pa^{-1} (8304 l day^{-1} $\times$ m^{-2} atm^{-1}) (666).

Silicone rubber is the only material used for drainage of the spinal fluid (677).

Artificial valves for the heart, including cold-cured, had saved 25,000 lives by 1970 (639). However, attempts to use PUR rubber for this purpose proved ineffective — the article degraded within the organism.

Silicone compositions are beginning to be used increasingly for making artifical organs; parts of the heart, kidneys, arteries and lungs (667).

Medical articles based on silicone rubbers have also a number of shortcomings: inadequate strength in repeated flexure (the membranes of an artificial heart withstand up to 40 mill. cycles of flexing, which is only one-tenth that necessary); the capacity of absorbing lipids from the blood (this causes swelling of the article and adversely affects its physicomechanical properties, and even in certain cases accelerates clotting of the blood when the flow is not rapid enough).

Auxiliary materials are used in medicine for electronic instruments which are inserted into the organism for brief periods and are covered with silicone rubbers.

For protection from excessive noise there may be used devices with parts made from a cured low-molecular rubber. The mix is inserted directly into the ear, which acts as the mould. As vulcanisation proceeds the organosilicon rubber takes on the shape of the ear, and, because of its flexibility, it can be extracted easily (633). To improve the sound-deadening a small lead disc is inserted into the silicone rubber before vulcanisation. The lead raises the mass of the article and increases the effectiveness of the protection from h.f. and l.f. noise.

In Soviet stomatology the impression materials Sielast and Sielast-69 (OST 64-2-47-70) are used to make impressions for recording defects of the jaws, the teeth and the soft parts of the mouth cavity. Organosilicon compositions curing at ordinary temperatures may be used as parting agents in making stomatological articles.

Similar materials are being produced outside the Soviet Union (639). Unfilled compositions based on low-molecular siloxane rubber are used for preservation of anatomical specimens (668). Polyorganylsiloxane coatings are used in making surgical instruments (669) and also for capsules for medicines (670,671). Because of their biological inertness certain advertised materials are used for food packaging (670).

Some research workers consider that with time there will be development of artificial hearts, kidneys, pancreatic and suprarenal glands, muscles, intestines and even the liver. There is hope of developing artificial eyes, which will restore elementary forms of vision to a blind person by means of electronic devices. It is reckoned that in time to come it will be possible to replace more than half the number of human organs by artificial ones.

OTHER FIELDS OF USE

By variation of the ingredients of silicone mixes it will be possible to produce vulcanisates with better than normal heat resistance (331,672), with high tear resistance, considerable compression resistance (649), and good dielectric properties (626) in conjunction with good thermal conductivity (497). There are fire-resistant, self-extinguishing (259,595), thermally conductive (347), translucent and semitranslucent (636 (?)), water-soluble (673), and oil- and petrol-resistant (347,595) vulcanisates. There have been produced also fire-resistant materials which do not swell in oils or fuel (674), and self-adhesive compositions (578).

We shall now consider the methods of using vulcanisates with modified (or improved) properties.

Cold-cured organosilicon rubbers may be used for a variety of coatings and linings (337,675,676), including adhesive, i.e. not requiring the use of bonding underlayers or primers (88,572,675). They may be applied to metals (662), plastics and organic rubbers (677), paper (676), polysulphone resins and wood (662), and metal wire and glass fabric (678). Silicone compositions may be recommended for treating textile materials with a view to improving crease-resistance, lengthening their wearing life, and making them resist dirt.

The Soviet compositions KLT-30 and Elastosil-11-01 may be used with good results in conjunction with polypropylene fabric to make footwear with improved moisture- and dirt-repellence, and also for treating fabrics and forming coatings on them (475). KL compositions may be used for sealing covers and gaskets for gearboxes.

The call for sealing and damping materials of low density led to the production of sponge rubbers of density 350—800 kg/cu.m or below, produced on site at from 10 to 25°C. These may have self-extinguishing properties (602).

There have been developed a series of sponge materials which are resistant to high temperatures, sunlight, moisture, radiation and oxygen, and having adhesive properties (636). We must point out the variety and constant widening of the available range of these materials. By varying the components it becomes possible to vary within wide limits not only the properties just mentioned but also the electrical, thermal and other properties (within, of course, definite limits). For instance, the volume resistivity may be varied from 10^3 to 10^{15} ohm cm, the thermal conductivity from 7.5 to 35.5 $Wxm^{-1} \times K^{-1}$ (4.18 and 19.7×10^{-4} cal $\times$ $cm^{-1} \times sec^{-1} \times {}^{\circ}C^{-1}$ respectively), the electric strength up to 27 MV/m, or kV/mm, the heat resistance to 350°C or somewhat higher, the low-temperature resistance to —100°C or better, the vapour permeability to 2.5—25 $\times$ 10^3 m(sic) $\times$ $day^{-1} \times Pa^{-1}$.

The low shrinkage of articles of low-molecular silicone elastomers (tenths of one %) makes it possible to use them for making moulds, moulding materials, and castings from polymers, or low m.p. metals or alloys of these (44,595). Moulding materials are particularly extensively used in countries with a highly developed fine castings industry, in particular in W. Germany. For making rapid and accurate castings from alabaster, wax, polyester and polyepoxy resins, plastics, low m.p. metals, the production of valuable reproductions of various kinds of impressions (including uses in forensic science) there may now be used in place of plaster of Paris, wax or gelatin cold-curing moulding compositions based on silicone-rubber and other ingredients. (Throughout confusion exists re moulds and mouldings, etc. Transl./Ed.).

For the preparation of moulds and articles it is useful to employ patterns of ordinary materials such as wood, metals, synthetic polymers, gypsum, stone or wax. As a rule parting agents are not necessary. For repeated moulding it is recommended to spread the moulds with a thin layer of vaseline. On porous patterns of gypsum or wood there is first applied a thin layer of varnish (quick-drying varnishes based on synthetic resins, as well as on shellac, are useful). In this way we can prevent mechanical sticking of silicone rubber to the surface of a pattern. When using mechanically weak patterns it is advisable to test beforehand on a small piece of the surface whether or not it is damaged in moulding, and also whether the vulcanisates comes away properly from the pattern (633,679).

For moulding there may be used fluid, viscofluid or, in some cases, paste-type organosilicon compositions. After vulcanisation the moulding compositions give soft moulds, easily transported in the made-up state. Paste-type compositions may be applied to a pattern by hand or with a spatula. Such compositions should be used only for modelling the coarser relief of a surface.

The most suitable for moulding mixes are two-component potting compositions. On parts where a copy has to be taken from one face we make a rim along the edges, e.g. of plasticine, and carefully pour the prepared composition over the surface. In moulding relatively small patterns the 'body' of the vulcanisate is sufficient to ensure shape retention in the moulded article. It is possible also to produce complex multi-component moulds.

The parting agents were greases, oils, vaseline, solutions of organic rubbers or resins in low b.p.

solvents, soaps and other anti-adhesives. The use of parting agents makes it possible to obtain mouldings from cold-curing siloxane compositions in moulds made from siloxane vulcanisates.

In the moulding of larger parts it is desirable to reinforce the material of the mould with a glass fabric or other textile material. To get sufficiently strong attachment of the fabric to the material of the mould, the fabric is impregnated with trichloroethylene, methyltriacetoxysilane etc. As a rule, the flexibility of the reinforced moulds is reduced. Nevertheless at the same time the strength is improved significantly. For use at high temperatures the walls of the moulds are reinforced with a ceramic, or refractory, or electrodeposited coatings and so on (595).

When wooden patterns are used we do not need any preliminary mechanical treatment in the majority of cases. The cleaned and dried surface is covered with an antiadhesion underlayer and is dried at room temperature until the tackiness disappears (679). Then we apply an organosilicon composition which has been carefully mixed with the curing agent. After full cure the pattern is removed from the mould, which can then be used to make fresh parts. The optimum physicomechanical properties of the mould are achieved after it has been stored for 4—6 days at room temperature. Then two wax castings are effected in it. The layer of wax left on the inside surface of the mould improves the resistance of the material to monomers and polymeric materials which are poured into the mould (such as styrene or polyester resins), and the parting effect is enhanced.

The service life of a mould is extended if the curing of the mouldings is carried out at room temperature. If the curing is effected at a raised temperature, it is useful to effect a preliminary heat treatment of the mould, e.g. by gradual heating in a drying cabinet. It is recommended to start the heat treatment at 80°C, and then to raise the temperature by 10°C each hour, until it reaches the temperature of employment of the mould. After cooling the mould is treated with wax.

It is possible to use silicone moulds to produce mouldings of gypsum, wax, casting resin, polyesters, PURs or other materials (680). Those of wax or gypsum have no odour and are suitable for making art objects, dental moulds, or death masks (501). In making wax mouldings it is recommended first to heat the mould to the m.p. of the wax so as to ensure that it flows readily into narrow slits. Fairly often the surface of moulds cast in wax has a flaky character. After careful washing with trichloroethylene and drying the moulds are once again ready for use.

When polyester or epoxy moulding compositions are used the parting properties of the siloxane rubber suffer. Not all the commercial casting resins give good quality articles in moulds made from cold-curing organosilicon compositions. Moulds which part with difficulty from the patterns are used only for making a small number of parts and prototypes. It is often possible to get better parting if the clean surface is treated in addition with a polydimethylsiloxane oil.

As indicated above, mouldings are made also from low m.p. metals and alloys. In this case the m.p. of the alloy or metal which is in contact with the silicone mould must not exceed 300°C. To achieve good flow of the metals, the preheated moulds are powdered with a fine metallic powder, silicon carbide or zircon. For mouldings of metal it is more suitable to use thin-walled moulds, to which a coating with good thermal conductivity is applied.

Moulds of silicone compositions may be used also to produce electroplated plastics, since electrolytes do not damage this sort of rubber. The only electrolytes ruled out are strongly acidic or strongly alkaline, particularly if the temperature is above 50°C.

Moulds of organosilicon compositions may be used to produce parts of dimensions larger than the pattern. To do this we first shape the initial pattern. After vulcanisation the pattern is placed for 2—3 h in trichloroethylene, under the action of which it increases in volume. The swollen model is then covered completely with gypsum so that the solvent absorbed does not evaporate. After hardening we get a gypsum impression measuring larger than the pattern. If this process is repeated a number of times, it is possible to get repeated enlargement of the part.

There are also useful moulding compositions which change colour according to the degree of cure (633).

Bonding agents and sealing agents based on low-molecular siloxane rubber may be used to seal cracks and joins in distillation columns. In this way we get a solid flexible coating which withstands the expansion and contraction stresses in the starting and turning off of the apparatus, as well as the various weather conditions (645).

Organosilicon sealants may be used for the protection of evaporation installations operating by solar energy (633). Their service life is a guaranteed 20 years. Silicone coatings do not fail under the action of heat, even if the installation becomes dry. They resist chemical reagents, they are non-toxic, and do not impart any odour to the water. In case of mechanical damage the coating is easily repaired in situ. The long service life in a moist atmosphere is turned to account in boat-building and for interior lining of refrigeration chambers. A mixture of silicone sealants and coaltar pitch may be used to protect the top bitumen facing of bridges, airport runways, gaskets and jackets of industrial plant, and for the protection of these against oxidation and degradation under the action of petrol, oil, water and the like (157). Coatings used to repair damage to chemical installations harden rapidly, are extremely strong, and where necessary can easily be removed.

Organosilicon compositions cured under ordinary conditions may be used in applying engraving on a glass vessel (633). To do this a 'mask' is taken from the original by applying a paste-form composition to the original. The pattern is imprinted on the rubber. Then the flexible mask is easily removed and applied to a different specimen, which is engraved in turn.

Heat-resistant organosilicon coatings with long service life at 150—200°C make it possible to eliminate considerable difficulties in anticorrosion protection of materials (661).

For the storage of powder-form carbonates and bicarbonates of alkali metals, which are used for fire extinguishing, their surface may be covered with a thin layer of a cured silicone composition.

Organosilicon compositions are used also for protective screening against radiation and high energy. They are used, in a mixture with radioactive compounds, as radiation sources (681). They may be used in fingerprinting etc., and for consumer goods (629).

Sealants of silicone rubber may be used for the storage in a clean state of equipment used in the food industry. For instance, Silastic RTV-732 is used in joins of panels and shelves, in glass doors, in kitchen tiles, and kitchen extraction ventilation. A similar sealant, white in colour, is used in refrigerators for sealing metal-to-metal joins and between the plastic and the lining of a refrigerator (633). Particular interest attaches to compositions which do not require the use of an adhesion underlayer, which are used for bonding. Basically these are single-component compositions which are applied to the surface of articles and which cure in air (629). Silicone compositions which have adhesion properties may be joined by vulcanisation to the surfaces of many materials (Dacron, Teflon, nylon, aluminium, copper, steel etc.).

The combining of copper foil and silicone composition makes it possible to make foil-laminated sheet. There are accounts of the use of silicone adhesives for attaching metal parts of a telephone to plastics parts.

Fluid silicone compositions may be used as anti-adhesion coatings for returnable packaging for the storage and transport of low-molecular organic rubbers (638). Loss of pressure-tightness in vacuum systems may easily be avoided by applying a silicone sealant in an aerosil container. After the removal of the solvent there is formed a film which is stable in service at 250°C and resistant to the action of solvents and chemical reagents. Thin membranes based on block copolymers containing polyorganylsiloxane and polycarbonate blocks may be used to make artificial breathing apparatus making it possible to remain under water for long periods.

Cold-curing organosilicon compositions may be used to give conveyor belts anti-adhesion properties. To do this there is applied a layer of thickness 6.3 mm which vulcanises within a day.

The resistance of organosilicon sealants of high hardness (85 Shore A) to printing inks makes it possible to use them to make printing rollers for the application of relief colouring to plastics, or intermediate layers for silk-screen printing, or for heat-resistant paints (614,682).

There are constant references published outside the Soviet Union to new types of silicone sealants, which not infrequently are little different from any others. However, there are sometimes references to interesting novel developments. For instance, General Electric's RTV-30 has a tensile strength of 5.3 MPa (53 kgf/sq.cm) and low shrinkage, 0.2% (683). Among new compositions curing at ordinary temperatures there are Eccosil 4853, which has superior tear resistance, and the paste-type compositions Silcoset (673) and Silastomer 70, which make it possible to vary the pot life (retaining fluidity) and rate of cure by altering the amount of catalyst (3—20 pbm). In the latter case accurate metering of the catalyst is not strictly obligatory. The physicomechanical and electrical properties of these cold-curing compositions are given in the Appendices.

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APPENDICES

Table 1 Properties of organosilicon compositions and sealants produced in the U.S.S.R.

Property	Compositions									Sealants								
	KL-4	KLSE	KLT-30	KLT-50	KLVAE-105	KLVAE-155	KLVSE-305	KLF-20	KLFS-30	Viksint U-1-18	Viksint U-2-28	Viksint U-4-21	Viksint K-18	VGO-1	Silpen	Elastosil P-1	14s-1	14s-2
Colour	Trans-lucent colour-less	Red	White		Red			Grey		White	Pink	—	—	White		White to grey	—	—
Density, kg/cu.m	1000	1150	1150	1300	1050	—	—	—	1300	2200	2200	1350	1100	1900	600	1900	1450	1400
Working temperature range, °C	-60—+200 incl.	-60—+300 incl.	-60—+300 incl.	-60—+330 incl.	-60—+250 incl.	-60—+250 incl.	-60—+250 incl.	-75—+200 incl.	—	-60—+300 incl.	-60—+300 incl.	-60—+300 incl.	-60—+250 incl.	-60—+250 incl.	-60—+200 incl.	—	-60—+250 incl.	-60—+250 incl.
TM-2 hardness (=Shore)	—	50—70	60—70	55—70	60—70	50—65	60—70	—	—	50—60	40—50	40—50	50—60	20	—	—	—	—
Tensile strength MPa	1—3	1—1.5	0.8—1.2	1.2—1.8	0.7	1—1.5	1.5—2.5	0.3—0.6	—	2	1.8	—	—	1.5	—	1.6	—	—
kgf/sq.cm	10—30	10—15	8—12	12—18	7	10—15	15—25	3—6	—	20	18	—	—	15	—	16	—	—
Elongation at break, %	100—140	80—140	120	120	110	130	130	100—130	—	160	200	—	—	150—600	—	140	—	—
Pot life, min*	10—40	15—40	15—40	15—40	20—35	15—30	15—30	15—40	—	30—35	3—8 h	0.5—5 h	0.5—6 h	10—30	—	—	0.5—3 h	2—5 h
Volume resistivity at 20°C, $\rho_V \cdot 10^{-13}$, ohm·cm, not above	10	—	1	—	1	1	1	10	—	1	0.5—5	5	1	3	10	10	—	—
tan δ at 1 MHz, not above	0.005	0.012	0.01	0.02	0.015	0.01	0.01	0.005	1.1	0.02	0.2	0.005	0.02	0.003	0.02	0.04	0.004	0.25
Permittivity at 1 MHz	3.2	4.1	3.4	4.5	4.0	3.2	3.5	3.2	3.1	6.5	3.9—4.5	3.5—4.7	3	3.8	2.9	4.0	5.4	5.8
Electric strength at 20°C, MV/m, or kV/mm	12.3	18	14.5	15	10	—	—	—	20.7	5.0	5.7—8.7	15—32	15	—	—	15.0	5.4	5.8

* Depending on the catalyst (temperature not stated Transl./Ed.)

Table 2 Properties of Dow Corning LTV polyorganosiloxane mixes

Property	Silastic																	Silgard						
	502	521	601	731	732*	733	735	382*	504	583	585	587	589	630	860	881	882	A*	B*	C*	D	E	G	182
Density, kg/cu.m	1120	1420	1290	—	1040	1360	—	1130	1470	1170	—	1380	1500		1470	1130	1130	1140	1380	1470	1500	1120	1100	1050
Viscosity																								
Pa·sec	50	12	30	25	25	10	—	5	25	14	—	30	30	10	30	50	50	14	30	80	30	60	80	5.8
P	500	120	300	250	250	100		50	250	140		300	300	100	300	500	500	140	300	800	300	600	800	58
Brittleness temperature, °C	—	—	—	−60	−73.3	−70	−60	−73.3	−60	—	—	—	—	−60	—	—	—	—	—	—	—	—	—	—
Shore A hardness	35	40	50	15—50	25	25	30—70	45	65	45	40	60	60	30—60	65	35	43	45	60	65	60	30	30—45	40
Tensile strength																								
MPa	5.45	2.81	2.11	3—7	1.05	1.09	1.5—5.0	2.81	4.56	2.81	2.81	4.2	4.2	2—5	4.57	2.11	2.81	2.8	4.2	4.57	4.22	4.9	5.98	6.32
kgf/sq.cm	54.5	28.1	21.1	30—70	10.5	10.9	15—50	28.1	45.6	28.1	28.1	42	42	20—50	45.7	21.1	28.1	28	42	45.7	42.2	49	59.8	63.2
Tear resistance, kN/m, or kgf/cm	1.4	—	1.4	—	—	—	8.7	1.7	7.1	2.6	—	5.3	5.3	—	—	—	—	2.7	5.3	7.1	5.3	6.3	19.6	—
Elongation at break, %	200	140	150	200—300	450	150—200	200—350	160	180	180	200	120	100	50—100	110	160	160	180	120	180	100	400	300—350	100
Volume resistivity, ohm·cm	—	—	—	—	—	—	—	—	—	—	—	—	—	—	$3\cdot10^{13}$	10^{14}	10^{14}	—	—	—	—	—	—	$2\cdot10^{15}$
Permittivity at 1 MHz	—	—	—	3.0—4.0	—	2.5—6.5	2.5—3.0	—	2.5—3.5	—	—	—	—	2.0—3.0	3.8	3.0	3.0	—	—	—	—	—	—	2.8
tan $\delta\times10^3$	—	—	—	2—5	—	3	1—5	—	1—5	—	—	—	—	2—3	47	15	15	—	—	—	—	—	—	1
Electric strength, MV/m, or kV/mm	—	—	—	16—18	—	18	16—21		15—20	—	—	—	—	15—20		13.97	13.97	—	—	—	—	—	—	13.9

* Thermal conductivity in W/m·K (or cal/sec·cm·°C) and the coefficient of (? volume Transl./Ed.) thermal expansion in $°C^{-1}$ are, respectively: Silastic-732—18.8 (or 0.45×10^{-3}) and 9.3×10^{-4}; Silastic-382 and Silgard A-21.7 (or 0.52×10^{-3}) and 7.5×10^{-4}; Silgard B and Silgard C-31.4 (or 0.75×10^{-3}) and 3.25×10^{-4}

Table 3 Properties of Rhone-Poulenc 'Rhodorsil' organosilicon compositions and sealants

Property	RTV-1053, CAF-1, CAF-4, CAF-5	CAF-3, CAF-4160, Thixo CAF-6, Thixo CAF-4	Mixtures																
			105	111	133	143	160	188	10321-121	10341-141	10347-147	10348-148	10351-151	10346-546	10547-547	10558-558	10550-559	10567-567	1063-132
Colour	—	—	Red	White	Red				Translucent colourless		Light brown		Trans-lucent colour-less	White	Red	Black	Pink-ish white	White	Trans-lucent colour-less
Density, kg/cu.m	—	—	1300	1180	1400	1500	1500	1500	1010	1010	1240	1230	1050	1210	1420	1000	1460	1400	970
Viscosity Pa·sec	10–25	25	10	16	30	10	55	90	1.1	3–4.5	150	7.5	4.5–6.0	16	40	2.5	70	35	6.0
P	100–250	250	100	160	300	100	550	900	11	30–45	1500	75	45–60	160	400	25	700	350	60
Thermal conductivity λ, W/(m·K)	—	—	31.2	27.1	37.3	5.4	31.2	4.70	24.0	16.7	29.1	29.1	16.7	34.2	37.0	—	6.67	4.15	15.6
λ·10 (sic), cal/sec·cm·°C	—	—	8	6.5	9.5	1.32	8.5	1.13	6.1	4.3	7.5	7.5	4.3	8.8	9.5	—	1.6	1	4
Hardness, Shore A	30–70	30–70	45	45	50	55	60	60	15	45	60	40	40–60	45	55	—	65	80	—
Tensile strength MPa	1.5–5.0	1.5–5.0	3.0	2.0	6.0	2.5	5.0	5.0	—	5–6	5.7	3.2	—	1.8	5.0	—	2.5	6.0	—
kgf/sq.cm	15–50	15–50	30	20	60	25	50	50	—	50–60	57	32	—	18	50	—	25	60	—
Tear resistance, kN/m, or kgf/cm	—	—	3.7	2.8	3.5	2	5.5	5.5		2	10–15	2.5	2	2	4.5	—	4	3.5	—
Elongation at break, %	200–350	200–350	140	180	4	100	130	130		160	200	210	125	170	150	—	110	85	—
Volume resistivity, $\rho_V \cdot 10^{-14}$, ohm·cm	—	—	3	3	1	3	4	3	7	10	2	2	6	7	4	5	8	10	1
Permittivity at 1 MHz	3.0–4.0	3.0–4.0	3.2	3.2	3.2	3.3	3.6	3.5	2.7	2.7	2.9	2.9	2.6	3.2	3.4	1.9	3.6	3.2	2.8
Electric strength, MV/m, or kV/mm	—	16–21	20	17	17	18	15	13	19	20	18	18	24	17	15	6	18	14	18

Table 4 Properties of SISS (France) organosilicon compositions and sealants

Property	RTV, single-component													Dispersions					
	501	502	521	589*	601**	860	881	882	S-5308	S-5335	S-5370*	5510	730	S-5313**	S-5314**	S-7037	S-7042	7306	7309
Colour	—	—	White	Red	White	Red			White		Beige	White		Brown	White	Red	—	—	—
Density, kg/cu.m	—	—	1420	1470	1290	1470	1130	1130	1130	1430	1100	1120	1050	1130	1130	1100	1050	1300	1100
Viscosity																			
Pa·sec	20—50	20—50	12	30	30	30	50	50	50	130	8	30	—	70	60	50	25	—	—
P	200—500	200—500	120	300	300	300	500	500	500	1300	80	300	—	700	600	500	250	—	—
Brittleness temperature, °C	-60	-60	—	-70— -60 incl.	—	—	—	—	—	—		-70	—	-73	-73	—	—	—	—
Thermal conductivity λ, W/(m·K)	—	—	29.1	29.1	17.8	29.1	20.8	20.8	20.8	—	4.2	—	—	—	—	—	—	—	—
$\lambda \cdot 10^4$, cal/sec·cm·°C	—	—	7.5	7.5	4.3	7.5	5	5	5	—	1	—	—	—	—	—	—	—	—
Hardness, Shore A	35	40—60	40—50	65	42	65	35	43	20	53	—	30	25	22	22	20	20	25	8
Tensile strength																			
MPa	3—6	3—6	3.5	4.5	2.1	4.5	2.1	2.8	1.2	3.85	—	2.4	1	0.83	0.83	1	1	1.7	0.8
kgf/sq.cm	30—60	30—60	35	45	21	45	21	28	12	38.5	—	24	10	8.3	8.3	10	10	17	8
Elongation at break, %	—	160—200	130—140	110—125	150	110	160	160	250	130	—	180	400	370	370	250	250	450	200
Permittivity at 1 MHz	2.5—3.5	2.5—3.5	3.5	2.5—3.5	3.45	3.7	2.9	2.9	2.9	2.9	1.17	—	2.8	3.0	3.0	2.5	2.8	—	—
$\tan \delta \times 10^3$	1—5	1—5	4	1—5	4.6	2.5	5	5	5	5	1	—	5	4	4	7	2	—	—
Electric strength, MV/m, or kV/mm	15—20	15—20	20	15—20	22	20	22	22	22	18	2	18	—	16	16	20	15	—	—

* Coefficient of thermal expansion 7.5×10^{-4} °C^{-1}

** Volume resistivity 3×10^{13} ohm·cm

Table 5 Properties of silicone compositions and sealants produced in the U.K.

Property	Silastosil			CCs 9159	CCs 9160	CCs 9161	2750	CCs 2446	Silcoset								
	A*	B	C						150	151**	152[3*]	100	103	102	104	105	201
Viscosity																	
Pa·sec	—	250	—	50–250	20–50	10–20	50–250	10–20	—	—	—	20–50	20–50	250	250	10–20	10–20
P	—	2500	—	500–2500	200–500	100–200	500–2500	100–200	—	—	—	200–500	200–500	2500	2500	100–200	100–200
Brittleness temperature, °C	-75	-60	-60	-60	-60	-60	-60	-60	-60	-60	-60	-60	-60	-60	-60	-60	-60
Hardness, Shore A	25	—	30–70	40–60	40–60	30–60	50–70	40–60	30–70	30–70	35	40–60	40–60	50–70	50–70	30–60	30
Tensile strength																	
MPa	1.41	—	1.5–5.0	2–5	3–6	3–6	—	—	—	—	—	—	—	—	—	—	—
kgf/sq.cm	14.1	—	15–50	20–50	30–60	30–60	—	—	—	—	—	—	—	—	—	—	—
Tear resistance, kN/m, or kgf/cm	—	—	—	1.25	0.53	0.26	—	—	—	3.5	7	—	—	—	—	—	—
Elongation at break, %	450	—	200–300	220	120	150	100–250	200–350	200–350	200–350	380	50–200	50–200	100–250	100–250	150–250	50
Volume resistivity, $\rho_V \cdot 10^{-15}$, ohm·cm	7	—	—	0.01	0.048	0.034	—	—	—	1	2	—	—	—	—	—	—
Permittivity at 1 MHz	-3.0 (sic)	3.0–4.0	3.0–4.0	2.0–3.0	2.5–3.5	2.5–4.0	2.0–3.0	2.0–2.5	—	2.8	2.95	2.5–3.5	2.5–3.5	2.5–3.5	2.5–3.5	2.5–3.5	2.5–3.5
tan δ, at (1?) MHz, $\times 10^3$	—	—	2–5	1–5	1–5	1–5	1–5	1–2	—	—	—	1–5	1–5	1–5	1–5	1–5	2–3
Electric strength, MV/m, or kV/mm	—	16–21	16–21	15–20	15–20	15–20	15–20	20–25	16–21	16–21	18	15–20	15–20	15–20	15–20	15–20	15–20

* Density 1020 kg/cu.m

** Density 1500 kg/cu.m; thermal conductivity 16.9 W/m·K (or 4.5×10^{-4} cal/sec·cm·°C)

3* Density 1070 kg/cu.m; thermal conductivity 16.8 W/m·K (or 4.4×10^{-4} cal/sec·cm·°C)

Table 6 Properties of Bayer silicone compositions and sealants

Property	SK-1, SK-3	SK-4	SK-5	56K	Abformmasse***		Giessmasse		Streich-masse	Knetmasse	Einbett-masse**	Elastosil			AP (sic)		Two-component composition	
												33*	34*	35	3406	2344**	Silo-pren K-1**	Silo-pren K-2**
Colour	—	—	—	—	—	Light yell-ow	White	Grey	Grey		—	Ivory	Grey	—	—	—	—	—
Density, kg/cu.m	—	1020	—	1200	—	1300	1500	1300	1200	1300	—	1150	1350	1000	—	—	—	—
Viscosity Pa·sec	—	—	—	—	20–250	—	20–50	—	—	—	20	—	—	—	—	250	10–20	250
P	—	—	—	—	200–2500	—	200–500	—	—	—	200	—	—	—	—	2500	100–200	2500
Hardness, Shore A	19–23	22–42	25	43	40–60	18	40	35	55	45	30–60	25	35	13	45	30–70	30–60	50–70
Tensile strength MPa	4.5–5	1.1–1.9	1.5	2.0	2–5	1.5	1–1.5	1.5	2.5–3	4–5	3–5	2	3	1	1.4	1.5–2.0	3–6	3–6
kgf/sq.cm	45–50	11–19	15	20	20–50	15	10–15	15	25–30	40–50	30–50	20	30	10	14	15–20	30–60	30–60
Elongation at break, %	500–700	600–700	400	200	50–200	450	50–100	120–350	50–200	320–350	50–200	350	200	300	140	200–350	150–250	100–200
Volume resistivity, $\rho_v \cdot 10^3$(? $\rho_v \cdot 10^{-13}$ Transl./Ed.) ohm·cm	0.5	—	—	3	—	1–5	—	—	—	—	2–3	0.9	9	5.2	3.8	2–5	1–5	1–5
Permittivity at 1 MHz	2.77–2.68	—	—	3.1	2.0–3.0	—	—	—	—	—	2.0–3.0	3.0	3.0	4.0–4.2	2.9	3.0–4.0	2.5–3.5	2.5–3.5
Electric strength, MV/m, or kV/mm	27	—	—	24–30	15.1–20.1	—	—	—	—	—	15.1–20.1	25	25	40	28	16–21	15–20	15–20

* Coefficient of thermal expansion 8×10^{-3} °C

** Brittleness temperature –60°C

*** No corresponding footnote! (Transl./Ed.)

Table 7 Properties of silicone sealants and compositions produced in E. Germany, Czechoslovakia, Japan and Italy

Properties*	E. Germany Chemiewerk (sic)			VCHZ Synthezia, Czechoslovakia, Lukopren							Japan				Italy, Sogesil	
											Shin-Etsu		Toray Silicone			
	6230	6232	6236	1692	510	1522	1725	8000	T1492	T1592, T1692	KE-10	KE-20	SRX-817	SRX-820	SH-9555	501, 502
Viscosity Pa·sec	25	10–20	5–25	25	10	10–20	5–25	2	25	25	—	—	—	—	—	2–5
P	250	100–200	50–250	250	100	100–200	50–250	20	250	250	—	—	—	—	—	20–50
Hardness, Shore A	50–70	30–60	40–60	50–70	30–60	30–60	40–60	30–60	30–70	30–70	49	51**			35	40–60
Tensile strength MPa	3–6	3–6	2–5	3–6	2–5	3–6	2–5	3–6	1.5–5	1.5–5	3.2	3.3	2.85	3.0	4.9	3–6
kgf/sq.cm	30–60	30–60	20–50	30–60	20–50	30–60	20–50	30–60	15–50	15–50	32	33**	28.5	30	49	30–60
Elongation at break, %	100–250	150–250	50–200	100–250	50–200	150–250	50–200	50–200	200–350	200–350	165	180**	197	100	400	50–200
Permittivity at 1 MHz	2.5–3.5	2.5–3.5	2.0–3.0	2.5–3.5	2.0–3.0	2.5–3.5	20–30	2.0–3.0	30–40	3.0–4.0	—	—	—	—	—	2.5–3.5
tan δ×10^3	1–5	1–5	1–5	1–5	2–3	1–5	1–5	2–5	2–5	—	—	—	—	—	—	1.5
Electric strength, MV/m, or kV/mm	15–20	15–20	15–20	15–20	15–20	15–20	15–20	15–20	16–21	16–21	—	—	—	—	—	15–20

* Brittleness temperature –60°C
** At 156°C

Table 8 Properties of General Electric RTV two-component silicone compositions and sealants

Properties*	11	21	30	41	60	77	88	90	91	560	577	580	602	615	616	630	631	632	634
Colour	White	Pink	Red	White	Red	White	Red	Red	White	Red	White	Red	Translucent colourless		Black	Blue	Blue-green		Green
Density, kg/cu.m	1180	1310	1450	1310	1470	1330	1480	1500	1180	1420	1350	1490	990	1020	1220	1280	1180	1240	1180
Viscosity Pa·sec	12	25	25	40	50	60	60	120	20	40	60	60	1.2	4.0	9.0	18	135	48	8
p	120	250	250	400	500	600	600	1200	200	400	600	600	12	40	90	180	1350	480	80
Coefficient of thermal expansion, $\alpha \times 10^6$	1.41	1.14	1.14	1.14	1.14	1.14	1.14	1.14	1.2	1.14	1.14	1.14	1.62	1.63	1.5	1.14	1.26	1.14	1.14
Thermal conductivity λ, W/m·K	7.15	7.56	7.56	7.56	7.56	7.56	7.56	7.56	6.3	7.56	7.56	7.56	4.2	4.6	6.7	7.56	7.56	7.56	7.56
$\lambda \cdot 10^4$, cal/sec·cm·°C	1.7	1.8	1.8	1.8	1.8	1.8	0.18	1.8	1.5	1.8	1.8	1.8	1.0	1.1	1.6	1.8	1.8	1.8	1.8
Shore A hardness	45	50	60	50	60	50	65	60	45	60	50	65	15	35	45	70	68	55	35
Tensile strength MPa	2.4	3.9	5.3	3.5	5.6	3.5	5.3	5.3	2.46	5.6	3.37	5.6	0.7	6.46	6.46	5.97	7.0	4.9	2.8
kgf/sq.cm	24	39	53	35	56	35	53	53	24.6	56	33.7	56	7	64.6	64.6	59.7	70	49	28
Tear strength, kN/m or kgf/cm	2.7	5.3	7.1	5.3	7.1	4.5	7.1	13.4	4.5	8	4.5	7.1	1.8	4.5	4.5	16.7	17	9	3.6
Elongation at break, %	180	180	130	200	130	220	110	150	180	160	180	110	200	150	125	300	190	180	220
Volume resistivity, $\rho_V \cdot 10^{-15}$, ohm·cm	0.6	0.88	2.9	0.15	0.13	1	0.10	0.13	1	1	1	1	0.10	1	1	0.6	0.6	1	0.4
Permittivity at 1 MHz	3.6	3.4	4.0	3.8	3.7	4.0	4.0	4.0	4.1	4.4	4.1	4.1	3.0	3.0	3.0	3.2	3.1	3.1	3.1
tan δ at 1 MHz	—	—	—	—	—	—	—	—	—	0.006	0.006	0.006	0.001	0.001	0.001	0.019	0.023	0.012	0.028
Electric strength, MV/m, or kV/mm	5.0	5.0	4.75	5.0	5.0	4.75	4.5	5.0	5.5	5.5	4.85	4.70	5.0	5.0	5.0	5.0	5.0	5.0	5.0

* Storage life of the mixtures 6 months; the brittleness temperature of mixtures RTV 11, 560, 577 and 580 is −115°C, that of the others −59°C

Table 9 Properties of General Electric RTV single-component silicone compositions and sealants

Properties*	102	103	106	108	109	112	116	118
Colour	White	Black	Red	Transluc-ent col-ourless	—	White	Red	Transluc-ent col-ourless
Density, kg/cu.m	1070	1070	1070	1070	1070	1060	1090	1070
Viscosity								
Pa·sec	—	—	—	—	—	30	40	35
P	—	—	—	—	—	300	400	350
Shore A hardness	30	30	30	30	30	30	26	22
Tensile strength, MPa	2.46	2.46	2.46	2.46	2.46	2.1	3.1	3.16
kgf/sq.cm	24.6	24.6	24.6	24.6	24.6	21	31	31.6
Tear strength, kN/m, or kgf/cm	8	8	8	8	8	4.5	9	5.9
Elongation at break, %	400	400	400	400	400	300	350	430
Volume resistivity, $\rho_V \cdot 10^{-15}$, ohm·cm	3	3	3	3	3	2	2	2
Permittivity at 1 MHz	2.8	2.8	2.8	2.8	2.8	2.8	2.7	2.7

* Storage life 1 year; brittleness temperature −59°C; thermal conductivity 5.1 W/m·K (or 0.12×10^{-3} cal/sec·cm·°C); coefficient of thermal expansion 15×10^{-5} $°C^{-1}$; electric strength 5 MV/m, or 5 kV/mm