PRODUCTION, PROPERTIES AND USES OF SILICONES

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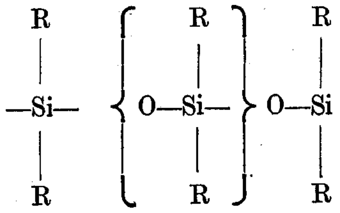
ABSTRACT

Silicones are polymers in which the backbone of the molecule is built up from alternate silicone and oxygen atoms and differ in many respects from all the other polymers in which the molecule is based on carbon-carbon chain. The methods of manufacture of different types of silicone polymers, their properties and specific uses with special reference to Defence equipment are reviewed.

Introduction

For a considerable time attention has been devoted entirely to polymers in which the skeleton is based on carbon-carbon chains only. This was but natural since carbon was the first and foremost element which could be made to link with itself a number of times to give the multiplicity of compounds which are dealt with under organic chemistry. Rapid developments, especially the epoch-making researches of Prof. F. S. Kipping of Nottingham University, U.K., carried out during the period 1899—1944, have laid a sound foundation in respect of polymers in which silicone is able to form long chains with alternating oxygen atoms.

Silicones are polymers in which the backbone of the molecule is not a carbon chain but is one built up from alternate silicon and oxygen atoms. Carbon is, however, present in varying proportions in these compounds and is in the form of different radicals directly linked to silicone atoms. Depending on the nature and number of monomers used for building the polymer molecules, the alkyl or aryl/silicone ratio varies and is one of the factors which influences the nature of the polymer. The nature and number of the monomeric silicone intermediates also determines the linear (I), cyclic (IIa and IIb), or cross-linked (III) structure of the resulting polymers.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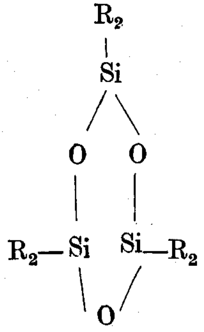
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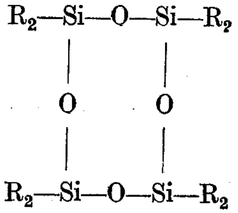
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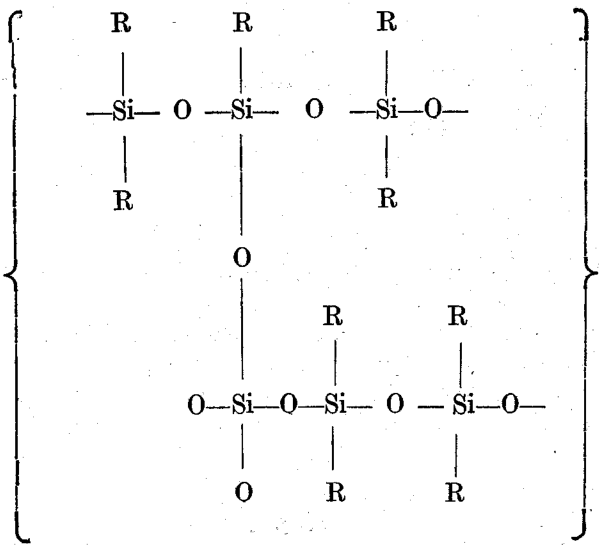


III

Alkyl, aryl, alkyl-aryl, and alkenyl substituted chlorosilanes are generally used as intermediates, and polymers of linear, cyclic, or cross-linked structure are obtained depending upon the use of di-, di-and mono- alkyl (aryl) chlorosilanes. The carbon-silicone distance in these polysiloxanes is exactly the same as the sum of the covalent radii whereas the silicone-oxygen distance is about the same as that found in inorganic silicates and is considerably less than the sum of the covalent radii. This indicates a rather highly ionic character of the siloxane bond in silicones. There is also considerable flexibility of the bond which is responsible for the freedom of motion of the organosilicone unit.

A study of such polymers by electron and X-ray diffraction, absorption spectra and supplementary deductions from molar refractivity and density, from flow properties and from heats of vapourisation, have shown that in the linear polymers there is very little obstruction to free rotation about the Si-O bonds and this results from the variation in magnitude of the bond angles in addition to the favourable geometry reducing steric interactions of attached groups. The low boiling points and the low temperature coefficients of viscosity of the linear polymers and the softness and flexibility of high molecular weight silicone rubber are attributed to the free rotation preventing the chains from packing sufficiently closely for the short range inter-molecular forces to be strongly operative[1].

The characteristic properties of silicone polymers in respect of flow and viscosity-temperature relationships is, therefore, explainable in terms of low intermolecular forces[2], high molar volumes and the small energy that is required for the motion. The freedom of motion of the organosilicone unit about the silicone-oxygen bond and the low intermolecular attraction distinguish polymers having organosiloxane chains from those having a framework of purely covalent bonds,

Preparation of Silicones

The preparation of silicone polymers is carried out in three definite stages; (*i*) preparation of organosilicone halides (*ii*) hydrolysis of an appropriate mixture of these intermediates and (*iii*) condensation or rearrangement of these polymers to achieve the desired molecular rearrangement. There are different methods which can be followed in the first step but the second and third steps are carried out in almost the same way irrespective of the method followed for the preparation of intermediates.

A simple method of making ethyl and higher alkyl chlorosilanes is the addition of chlorosilanes to olefines[3]. An example of this method is the preparation of ethyl trichlorosilane.

$$H_2C{=}CH_2 + HSiCl_3 \xrightarrow{Ag_2O_2} CH_3\ CH_2\ Si\ Cl_3$$

Ethylene can be obtained from ethyl alcohol and trichlorisilane may be made by the action of hydrogen chloride on silicone or ferrosilicon.

In addition to the above, Wuntz synthesis and metathetical reactions of silicone tetrachloride with zinc alkyls and mercury alkyls can be used. The most promising reactions from the point of view of suitability for large scale manufacture are (*i*) Grignard reaction and (*ii*) the reaction between alkyl or aryl halides and catalysed silicon metal.

(*i*) *Grignard method*—

If the preparation of the simple dimethyl silicone by this method is taken as an example, the reactions involved will be as follows, starting from the raw materials.

(*a*) *For* $Si\ Cl_4$—

$$SiO_2 + 2C \rightarrow Si + 2\ CO$$

$$Si + 2\ Cl_2 \rightarrow Si\ Cl_4$$

or $$Si\ O_2 + 2C + 2Cl_2 \rightarrow Si\ Cl_4 + 2\ CO$$

(*b*) *For* CH_3Cl—

$$CH_3OH + H\ Cl \qquad CH_3Cl + H_2O$$

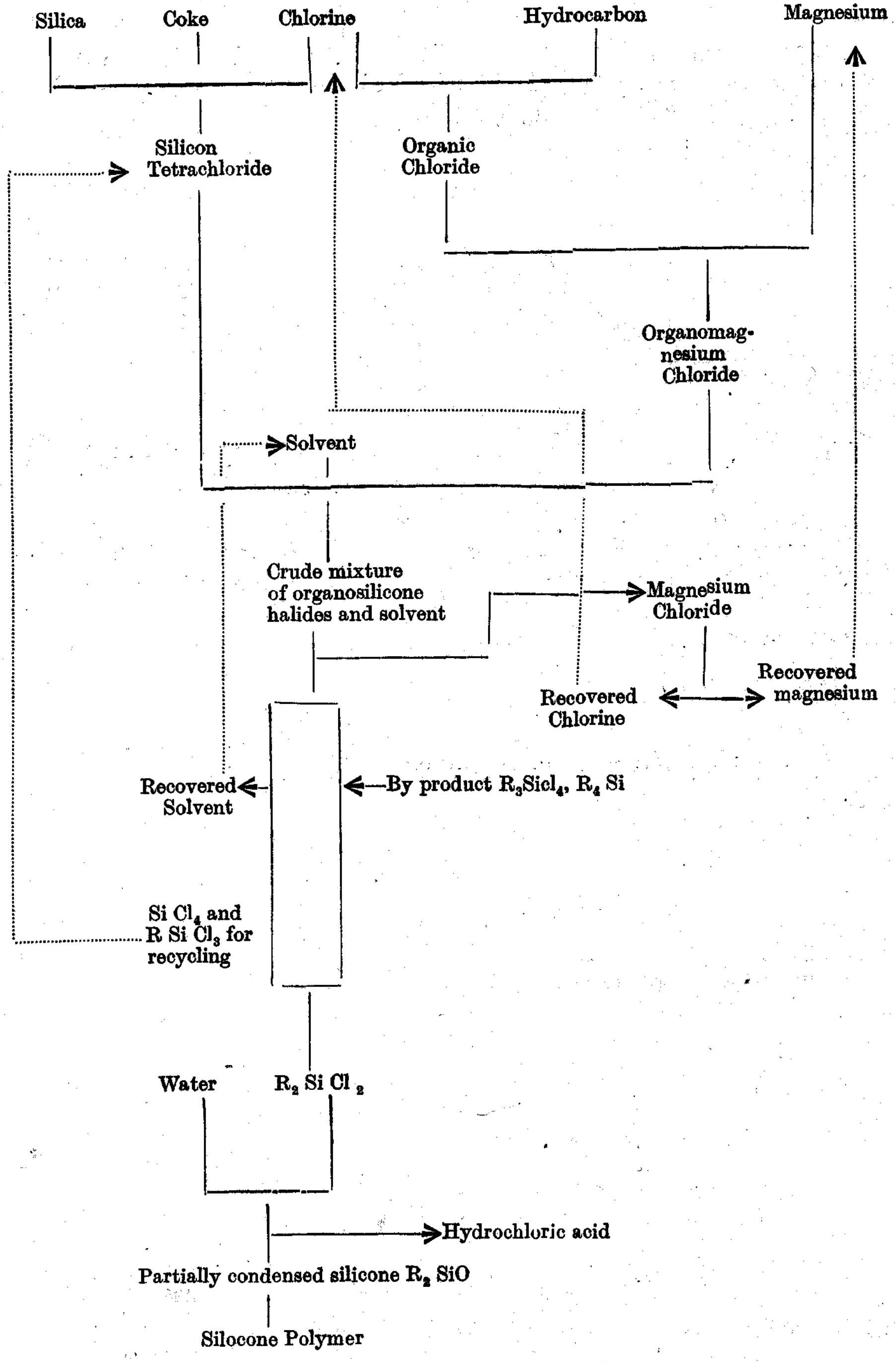
(*c*) *For Mg*

$$Mg\ Cl_2 (\text{Electrolysis}) \rightarrow Mg + Cl_2$$

or $$MgO\ (\text{with reducing agent B}) \rightarrow Mg + BO$$

Calculations show that free chlorine and free magnesium involved in the process represent 2·6 times the weight of methylsilicone produced. In the synthesis of phenyl silicone, however, a much larger part of the total weight of the reactants appears in the product. If. therefore, the cost of alkyl or aryl chloride is uniform and in case all other things are equal, the preparation of silicone with large organic groups costs less than the one with small groups.

Based on the above considerations, E.G. Rochow[4] indicated the following flow sheet :—



IV. Production of silicone polymers by Grignard method.

The Grignard process is extremely flexible in that compounds having a wide variety of organic substituents can be prepared by this method. However, equipment of a specialised design is necessary for handling highly inflammable solvents like diethyl ether and for handling the reaction products under anhydrous conditions. The cost of the product depends upon the multiplicity of steps involved and the use of silicon tetrachloride which contains only 16 per cent of silicone.

(*ii*) *Direct process*—

In this process copper to the extent of about 10 per cent is added to silicone and alkyl halide is passed over this material at about 275° C which results in the formation of alkyl silicone halides. Copper serves as a catalyst in this reaction. The various steps involved in such a reaction are as follows when the starting materials are also taken into consideration.

$$Si_2O + 2\ C \longrightarrow Si + 2CO$$

$$CH_3OH + HCl \longrightarrow CH_3Cl + H_2O$$

$$2CH_3Cl + Si \longrightarrow (CH_3)_2SiO + 2HCl$$

$$SiO_2 + 2C + 2CH_3OH \longrightarrow (CH_3)_2\ SiO + H_2\ O + 2CO$$

The two moles of hydrogen chloride required for the preparation of the required quantity of methyl chloride are liberated at a later stage by the hydrolysis of dimethyldichlorosilane. Consequently two moles of hydrogen chloride circulate in the process.

In this direct process, conditions of reaction can be adjusted in such a way that dimethyldichlorosilane is the main product but other substitution products are invariably formed and have to be separated from the main product.

For the preparation of aryl silicone halides by this method a different set of conditions have to be used. Silver is used as a catalyst and higher temperatures of the order of 375° to 425°C have to be employed. Excess of chlorobenzene is used in the preparation of diphenyldichlorosilane and it acts as a diluent and sweeps through the high boiling phenylchlorosilianes^5. The reactions involved are as follows:

$$SiO_2 + 2\ C \longrightarrow Si + 2\ CO$$

$$C_6H_6 + Cl_2 \longrightarrow C_6H_5\ Cl + HCl$$

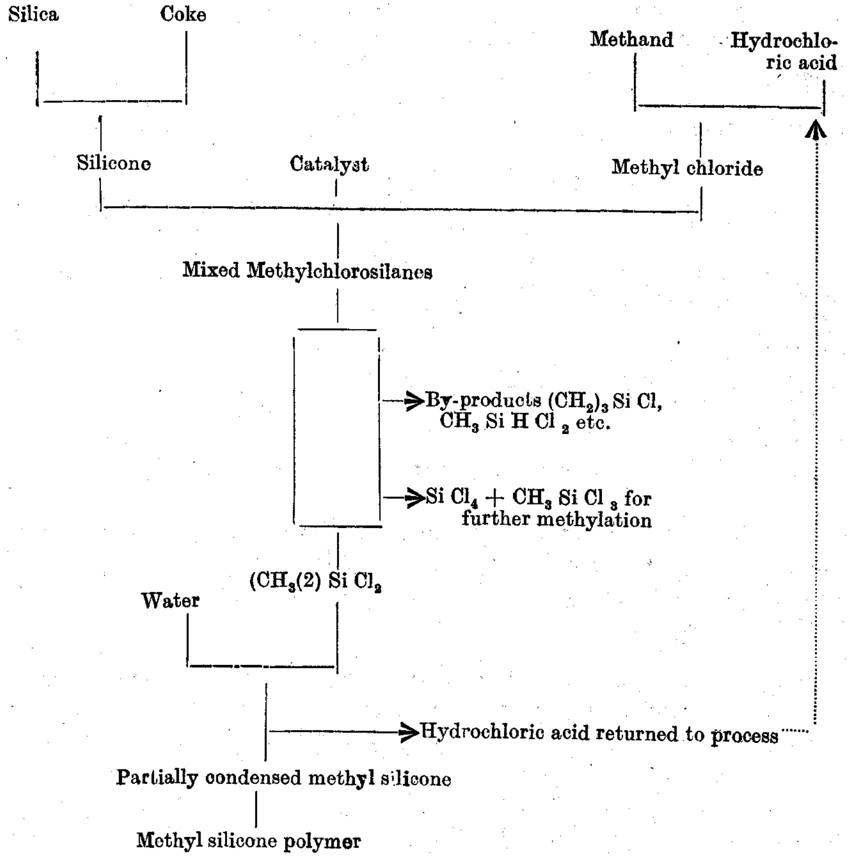
$$2\ C_6H_5Cl + Si \longrightarrow (C_6H_5)_2\ SiCl_2$$

$$(C_6\ H_5)_2\ SiCl_2 + H_2O \longrightarrow (C_6H_5)_2\ SiO + 2\ HCl$$

$$SiO_2 + 2C + 2C_6H_6 + 2\ Cl_2 + H_2\ O \longrightarrow (C_6\ H_5)_2\ Si\ O + 2\ CO + 4HCl$$

As in the case of the Grignard method, here also, the basic material cost for phenyl silicone would be less than that for methyl silicone. But, in this case, the cost of recovering the silver catalyst will be high and the hydrochloric acid cannot be easily recirculated in the process.

The flow sheet suggested by E. G. Rochow[6] for the preparation of methyl silicone by the direct method is given below:



V. Production of methyl silicone by the direct method.

In the processing of alkyl or aryl silicone halides the operations and processes like distillation, hydrolysis, condensation, and curing are common. Since the boiling points of some of the alkylchlorosilanes are very near each other and since some of them form azeotropes[7] the distillation column should function at a very high efficiency[8]. Storage, fractionation and transfer manipulations have to be carried out under anhydrous conditions. In addition, precautions have to be taken against accidents due to the highly volatile and inflammable nature of compounds like methylchlorosilanes[9].

Hydrolysis of alkyl or aryl chlorosilanes can also be carried out under different conditions and the equipments should be able to withstand the high concentrations of the acid produced. The process of hydrolysis has also to be controlled so that a balance is maintained regarding the quantity of acid that can be recovered and the extent of equilibrating action of the acid on the alkyl or aryl silanes that are being formed.

As far as further processing is concerned, silicone elastomers can be processed in the equipment that can be used for compounding and curing of natural rubber. The processing equipment for curing the resins should, however, be able to withstand the high operating temperatures used.

Silicone fluids

Methyl silicone fluid is of interest both from the theoretical point of view and the practical advantages of the material. Dimethyl-dichlorosilane is hydrolysed with water when the resulting silicol at once condenses with itself to form cyclic polymers and linear condensates. The product is a colourless oil which contains varying proportions of different polymers having varying boiling point, vapour pressures and freezing points. To reduce the proportions of the low boiling polymers, a procedure known as catalytic equilibration is adopted. Some of the equilibration catalysts are acqueous sulphuric acid, ferrie chloride and potassium hydroxide[8].

The same procedure can be applied to branched chain systems also. Silicone oils of the chain stoppered type derived from dialkyldichlorosilane and trialkylmonochlorosilane by the equilibration method can be made in different ranges of viscosity. All these silicone oils are thermally stable and are resistant to oxidation. Their most important property is the small change in viscosity with temperature. [11] All the methyl silicone oils are soluble in benzene, toluene, carbon tetrachloride, chloroform and ether. They are only partially soluble in acetone and lower alcohols. Oxygen has no effect on them upto about 150°C, and hence there is no sludging or discolouration or acid formation. At 200°C, and higher temperatures, there is oxidation in the presence of air[12]. In a closed or evacuated system, however, the upper temperature limit is only the point of thermal depolymerisation which is between 350°C and 400°C[13]. Silicone oils have no chemical action on iron, copper, aluminium, tin, lead, cadmium or chromium. They are not affected by dilute acids (except hydrofluoric acid) and dilute alkalies. They are, however, attacked by strong acids and alkalies. The introduction of chlorinated phenyl groups in the low molecular weight polysiloxanes had produced fluids with substantially better lubricating properties. Replacement of methyl groups by hydrogen increased their reactivity and fluids of these types can be gelled at relatively low temperatures in the presence of metal salts of fatty acids. Such fluids are used for imparting highly durable water repellent finishing to textiles[14].

Silicone greases, made from silicone oils are disperse-two-phase systems which furnish controlled amounts of silicone oil under conditions where a liquid lubricant would be inappropriate. The greases are made either by conventional techniques or by special methods which are intended to preserve the special property of silicones in respect of their resistance to high temperature. The solid phase can be silica aerogal[15] to give a soft jelly with excellent electrical properties or lithium stearate soap[16] to give a lubricant for heavy duty bearings.

Silicone resins

Three of the different methods adopted for making methyl silicone resins are as follows—

(*i*) Dimethyl silicone is prepared by hydrolysing dimethyl-dichlorosilane or its esters followed by catalytic oxidation[17].

(*ii*) Dimethyl-dichlorosilane is mixed with methyltrichlorosilane or silicone tetrachloride and then hydrolysed and the products condensed.

(*iii*) Using the Grignard reagent, silicone tetrachloride is partially methylated and the mixture of products obtained hydrolysed directly.

In all the above processes, the CH_3/Si ratio has to be very carefully controlled. Each method has, however, its own advantages. Control of final viscosity, preparation of rapidly curing resins, and time required for the curing of the resins are some of the factors to be considered while selecting any particular method to prepare a desired resin.

The drying or curing of methyl silicone resins can be effected by phosphorus pentoxide[18], sulphuric acid[19], by heating or activation with infrared or ultraviolet energy or by catalysts containing lead, iron, cobalt and zinc. The degree of cross linking encountered is less than what is expected and this is ascribed to the loss of potential cross links by cyclisation reactions which are thought to be facilitated by the flexibility of the O-Si-O bond angle[20].

Methyl silicone resin does not decompose to a carbonaceous residue. When the temperature of a machine in which methyl silicone is used as electrical insulation[21] exceeds the recommended higher temperature limit for the insulation, the material does not char as would a substance having carbon-to-carbon structure but it simply oxidises superficially to silica.

Low molecular weight methoxylated silicone resin may be made to react with glycerol and then with phthalic anhydride. Ether exchnage can also be carried out with phenolic and epoxy resins. The resulting copolymeric silicone alkyds, silicone-phenolics and silicone-epoxies have excellent heat resistance, better adhesion to copper and improved brushability. These resins have also good electrical properties and water repellency [20].

The Et/Si ratio of the resin has to be carefully controlled in preparing commercially useful resins. The resins derived from higher alkysilanes cure more slowly and remain softer in consistency than methyl silicone resin. The higher alkyl silicones are necessarily higher in organic content than a comparable methyl silicone and are influenced to a corresponding lesser extent by the siloxane net work. The higher alkyl silicones also oxidise more readily than the lower members of the series.

The siloxanes that contain unsaturated alkyl groups form a special class of polymers as their polymerisation can take place through the organic part of the molecule as well as through the siloxane groups. When heated with air or with peroxide catalysts vinyl and alkyl siloxanes polymerise. Such resins can also copolymerise with some organic allyl and vinyl compounds[22].

An aromatic radical substituent in a siloxane, however, alters the properties of the siloxanes to a considerable extent. Its reactions of and conditions of polymerisation are entirely different from those of methyl siloxane. For example, diphenyldichlorosilane on hydrolysis gives diphenylsilanediol but not a condensed siloxane as in the case of dimethyldichlorosilane. The diphenylsilanediol is so stable against self-condensation that even when warmed with acid it yields only a trimer and when warmed with alkali it yields only a tetramer. The diol condenses further only at 100°C and the condensation can be made to proceed rapidly by heating it at 200°C or higher. The resin that is formed remains weak and brittle when cold and softens at a moderate temperature. It burns readily with a sooty flame but it is remarkably resistant to oxidation in that the polymer can stand 400° to 500°C in air for several hours.

One of the methods by which the phenyl silicones can be modified is by chlorinating the phenylchlorosilane. The conditions of hydrolysis and further condensation of such chlorophenyl-chlorosilanes are similar to those of the corresponding unsubstituted compounds. If an average of three chlorine atoms is introduced into each phenyl nucleus the product becomes non-flammable. These chlorinated phenylsilicones are highly resistant to oxidation, are thermally stable upto at least 450°C and have very good electrical properties. Corresponding fluorinated phenylsilicones form stable flameproof resins for service at elevated temperatures.

The brittle, vitreous and soluble nature of the phenyl-silicone resins can be overcome by introducing alkyl and aryl groups into the some chlorosilane so that both the substituents are linked to the same silicon atom or by co-condensing alkyl and aryl silicols to obtain a copolymer[23]. The composition of the copolymer can thus be varied over a wide range. The mechanical strength and toughness of the copolymer exceed those of either polymer when taken alone, without any simultaneous deterioration in other properties. The dielectric strength of glass cloth coated with such resins is excellent even upto 300°C. Ethyl phenyl silicones have service temperature which is about 50°C lower than that of phenyl methyl silicones.

Silicone elastomers

Methyl substituted chlorosilanes are the simplest type of silanes used in the preparation of silicone rubbers. For this purpose, very carefully purified dimethyldichlorosilane, from which compounds with trifunctional groups have been carefully removed, is hydrolysed. The hydrolysis product is treated with small amounts of iron chloride or sulphuric acid or sodium hydroxide. The resulting gum which is formed by the building up of elastomeric aggregates, without cross-linking or galling, is washed free from the above reagents. It is then milled with inorganic fillers and a curing catalyst on mixing rolls. Further curing results in an infusible and insoluble elastic material. Silicone rubber has exceptional thermal stability. Service over long periods at 150°C does not destroy its elasticity[24] and permanent compression set is low. It has excellent electrical properties. The elasticity and softness persist down to —55°C without the addition of plasticisers.

The tensile strength, maximum elongation and tear resistance of a straight silicone rubber are poor as compared to natural rubber[25]. By using newly developed fillers like Aerosil, prepared from silicon tetrachloride, rubber with very low water absorption and a tensile strength of 600—1200 psi. are produced. Treated fillers give unusually high tensile strengths of 1200—2000 psi. In vinyl substituted rubbers the case of cure is increased and there is a marked improvement in the compression set of cured rubber. In addition to the characteristic thermal stability of silicone rubber, addition of polytetrafluoroethylene gives improved tear strength, oil resistance and good compression set properties.

Introduction of polar groups into the polysiloxane molecule like trifluoropropyl or cyanopropyl groups markedly increases the resistance of the rubber to non-polar oils and solvents as compared with conventional silicone rubbers[14]. The cyano group at β— or γ— positions increases the oxidative stability over that of the parent alkyl group or of α—substituted structures. In structures having γ—cyanoprophyl group the oxidative thermal stability is of the same order as that of methyl silicone and compositions containing more than 35 per cent of γ—cyanopropylsilicone, the rest being dimethyl silicone, show with various solvents volume swelling of the same order as some of the more solvent resistant organic rubbers[26].

Silicone rubbers having unsaturated groups cured at low temperature and at atmospheric pressure do not show any porosity. Crosslinking can be made to take place at unsaturated linkages and at other points also. Free redicals obtained from benzoyl peroxide or its 2:4-dichloro-substitution product are used for this purpose. Fillers used must be inert, stable to high temperatures and of fine particle size [25].

The curing of different types of silicone rubber has been studied in great detail [27]. Whereas the number of useful curing agents is strictly limited in the case of fully saturated structures, a wide field is opened up when polymers having vinyl groups are considered. Polymers with high vinyl content can be cured with sulphur or sulphur containing agents. Benzoyl peroxide, 2:4-dichlorobenzoyl peroxide and tertiary butyl perbenzoate can be used for curing both methyl and vinyl silicones while ditertiary butyl peroxide and dicumyl peroxide produce satisfactory cure with vinyl silicones only. When benzoyl peroxide is used, external pressure is necessary during set-cure to avoid porosity. There is, however, very little tendency to develop porosity when 2:4-dichlorobenzoyl peroxide is used. Ditertiary butyl peroxide is highly volatile but dicumyl peroxide is not. These two reagents, however, do not react with carbon blacks and hence can be used to cure conducting types of silicone rubbers.

Vinyl substituted silicone rubbers can be cured with sulphur. Both zinc oxide and stearic acid retard this cure.

Silicone rubbers can be cured cold by using a polysilicate and a metal catalyst such as lead or tin in the form of organo-metallic salts. The reaction can, however, be accelerated by temperature. These cold cured rubbers have much of the heat stability of peroxide cured rubbers but have poorer physical properties. These rubbers, however, find many specialised uses.

When high energy radiation (γ—radiation from Co-60 source) is used for curing silicone rubbers free radicals are produced. The physical properties of the product are similar to those obtained with conventional peroxide curing agents. Radiation cured rubbers have superior heat stability. Although carbon black, as filler, does not interfere with curing, it reduces the heat stability of the rubber. Silica filled compounds, however, yield heat stable rubbers.

Recent investigations have shown that replacement of methyl and phenyl groups in silicone by $-CHNH_2$, $-CH_2P(O)Cl_2$, $-C_6H_4OH$ and $-CH_2OOC.C(CH_3){=}CH_2$ improve their mechanical strength especially at high temperatures. These are not yet available commercially[14].

Silicone elastomer foams are produced from a mixture of liquid hydroxylated dimethyl polysiloxane, a similar polysiloxane, trimethyl blocked methyl hydrogen polysiloxane, diatomaceous earth and a tin salt $Sn(O_2CCH(Et)Bu)_2$[28]. Such foamed silicones are useful in thermal insulation where extremes of temperature are encountered.

A recent innovation is the preparation of fibrous silicone rubbers[29]. It has many of the properties of both foamed and sponge elastomers but unlike either, it contains a random veb-like arrangement of hollow filaments. Hollow filaments closed at both ends are first produced by forcing the silicone compound through a spray gun. The roll produced from the filaments is then cured in hot air. The compression deflected characteristics can be varied and the product has an excellent compression set. It offers very low resistance to air flow. This process can be used with any silicone rubber compound which forms a satisfactory dispersion.

The excellent properties of silicones (fluids, resins and elastomers) especially their thermal stability, resistance to oxidation, common solvents, chemicals and dilute acids, their hydrophobic nature, resistance to weathering, excellent adhesion to glass, ceramics and metals, form the basis for their wide use in different fields.

Uses of silicone fluids

Silicone fluids are effective in very small concentrations (of the order of 50 parts per million) as anti-foaming agents and find use in industry where excessive foaming interferes with the efficiency of operation. They are also used for imparting water repellency to textiles, leather, paper and ceramics, as a damping device, as dielectric fluids and in hydraulic systems. Their use as mould release agents in rubber and plastic industries has become extensive in industrially advanced countries.

The superior wetting and spreading properties of the fluids permit easy formation of a smooth, continuous, hydrophobic and non-oily film. Hence they are used in automobile and furniture polishes.

Water repellent finish can be applied to most textile fibres including synthetics, except wool. Silicone treatment imparts, in addition, stain resistance. The handle and drape of the fabrics are also improved. The finish is resistant to laundering and dry-cleaning. In the case of both textile fabrics and leather, water repellency property can be imparted to the materials without affecting their 'breathing' property.

Grease-like products are prepared by combining silicone fluids with suitable thickeners[30]. They function as a soft film lubricant and corrosion protectant. They are, therefore, used on the threads of mortar shell fuses. The product is well suited for this use since it maintains its grease-like consistency over the temperature range —65° to 160°F and does not affect the materials of construction. A waterproof, dielectric and non-melting grease which retains its consistency over the range —65° to 400°F is used in the tropic proofing of sparking plug elbows, for sealing aircraft ignition systems and electronic equipment.

Silicone fluids show little change in damping force over a wide temperature range or after long periods of time and hence are used as damping media in overload relays, dash-spots, torsional vibration dampers and delicate instruments. They are also used as transducer fluids with sound transmission characteristics similar to those of water.

As a heat transfer medium silicone fluids are used in liquid bellows and in heat treating and high temperature baths.

As an effective lubricant-protectant for ferrous alloy parts they are designed for application to threads of bomb, rocket, mortar and artillery shells. They provide excellent protection during indoor and outdoor storage.

The fluids are used for making greases which can be used in the temperature range —100° to 350°F. These greases are used in the bearings of small synchronous motors, meter clocks, plastic gears and electronic and mechanical instruments exposed to extreme temperatures and weathering. Pneumatic and high vacuum greases are also made from these fluids.

Silicone fluids are used as liquid dielectrics in capacitors, small transformers and electronic assemblies designed to give maximum life and reliability. They show little change in dielectric properties over a wide range of frequencies and temperatures.

Silicone fluids are used in a new system which controls the speed of the motor car engine fan when the engine is operating at high speeds[31]. They are used as damping media for camera mountings in jet aircraft. Valves used in rocket motor research contain silicone greases.

The properties of silicone fluids such as high compressibility, low viscosity/temperature coefficient and resistance to shear breakdown form the basis of their use in liquid springs in Dowty undercarriages of aircraft[32].

A mixture of siloxane oil and halogenated butane, butene, pantane, pentene or pentadiene is reported as a suitable material to inhibit combustion of dielectric liquids, damping liquids, lubricants and hydraulic fluids[33].

Uses of Silicone Resins

Silicone resins are used either alone or after modification with alkyds or phenol-formaldehyde resins of epoxy rosins. Silicone resins are stable up to 275°C and have high electric strengths, low permitivities and low power factors for over a wide range of frequencies. They form the basis of a new class of insulation that withstands high operating temperatures, frequent overload conditions. These properties are useful when there is limitation of space and high moisture resistance is required.

The silicone resins are used in bonding varnishes for mica, glass fibre and asbestos, in impregnating varnishes for electrical coils, motors, generators and transformers, as bonding resins for laminates, and in costing varnishes for glass cloth and sleeving. The main advantages of silicone impregnated insulation is that it permits an increased output per unit volume of motor. This is of special interest in cases where space is restricted as in aircraft.

Silicone laminates made from silicone resins are largely used for ducting components near the exhaust systems of jet aircraft where they can withstand operating temperatures of the order of 250°C. Radomes made of such laminates retain their strength at temperatures produced by frictional heat at high speeds and have suitable dielectric properties.

Silicone resins are used as dielectrics to increase the life and overload capacity of industrial and traction motors, generators, transformers, solenoids, lead wire and electronic parts and assemblies ^{35}. They are also used in wire and glass cloth enamels and varnishes. As potting compounds they are used to fill electric coils and caulk terminal outlets and commutator risers. These resins cure on heating.

Thermosetting resins are used along with glass fibres in the fabrication of aircraft brake assemblies and moulded parts for jet engines and aircraft ignition systems. The heat distortion temperature of such products is reported to be above 950°F.

Silicone modified polyester resins are based to bind mica flakes to glass fibre sheets to make mica tape for wrapping the conductor bars of generator coils ^{36}.

Heat stable tapes and films coated with pressure sensitive silicone adhesives are tacky and flexible within the temperature range—80° to 500°F. Their use in electrical insulation ensures long service. A pressure sensitive adhesive that can function within the range—50° to 150°C and which has improved adhesion on glass, polyethylene and polytetrafluoroethylene has been developed^{34}.

Silicone resin paint pigmented with aluminium used on exhaust chimneys can withstand outside weathering for long periods and also a temperature of 600°C.

Uses of Silicone Elastomers

Various types of elastomers are prepared from silicones and these elastomers are used specially when very high or very low operating temperatures are encountered. The purity of the monomer or monomers, molecular weight and type of substituent side group govern the properties of the product. Although a molecular weight of 10^6 gives optimum properties, in other respects the product becomes stiff. Normally products with a molecular weight of 10^3 are used.

Silicone rubbers are used in aircraft door and bomb bay seals. They are also used in jet engines where unusually high and low temperatures are encountered. Silicone rubber switch boots are proving useful at low temperatures and at relatively high ozone concentrations encountered in aircraft at high altitudes. Ducting made from glass cloth coated with silicone rubber is used in anti-icing and heating systems in aircraft.

Silicone rubber is employed as an insulator in power and control cables for naval use. Where the cable is damaged by fire it leaves a residual ash, the insulating value of which is normally sufficient to maintain communication until the ship reaches harbour. The life of the cable under extreme temperature conditions is greatly superior to that of normal cables.

Silicone rubber tubing is more resistant to repeated sterilisations by autoclaving than natural rubber and it is transparent and practically colourless. It is reported to be in the experimental stage for use as tubing in blood transfusions, Cold curing silicone rubbers find a variety of uses in electrical industry. Many small components are now encapsulated in them to ensure good performance under tropical conditions. Repairs can be effected by simple plugging and taping techniques. Dispersions of these rubbers can be used for preparing dip-coated tapes for electrical applications. Cold curing rubbers are finding some use as a dental impression material where their accurate reproduction of detail is an advantage.

Silicone rubber membranes are very much faster than any other film used hitherto for separation of mixtures of gases, like mixtures of nitrogen and oxygen or of carbon dioxide and oxygen[37]. Permeabilities for all gases were about 10 to 100 times as great as those of similar permeabilities for plastic films. Selectivity of silicone rubber membranes for the gases tested in the investigation is as good as that of the best ones available.

Silicone rubber is used for frames, cushions and seals around aircraft[38]. It is now the centre layer in 'safety glass' windshields for supersonic aircraft. Polyvinyl butyral cannot withstand the intense frictional heat generated by potential supersonic speeds. Silicone rubber laminates retain full strength and clarity at temperatures ranging from—65° to over 350°F. The shatter resistance of silicone laminated glass is less than that of the polyvinyl butyral laminate below 160°F but the former laminate is twice as strong as the latter above 200°F. The wide use of silicone elastomers as diaphragms, gaskets, seals, and tubing in jet aircraft is also indicated[39].

Elastomers made from a mixture of about 65% of γ—cyanopropyl substituted silicone and about 35% of dimethyl silicone polymer show high resistance to solvents and are promising as adhesives, solvent barriers, encapsulating compositions and automobile and aircraft components.

A silicone rubber which can be vulcanised at room temperature is used for coating and encapsulating electrical and electronic equipment[35]. A fluorinated silicone rubber used in cables and O—rings of jet planes swells in an aromatic test fuel by only about 20%, while ordinary rubber under the same conditions swells by as much as 200%.

The above review on silicones points to the possibility of increasing the efficiency of different types of equipment and maintaining that efficiency under extremes of temperature and humidity conditions. The various silicone compositions are however, at present imported and are very costly. For example, the silicone composition that is recommended for rendering leather waterproof without impairing its 'breathing' property, costs about Rs. 18 per pound and the cost of fluorinated oil-resistant silicone rubber that can function over a wide temperature range is about £15 per pound. It will, however, be advantageous if investigations are undertaken to develop and produce at least some silicones for meeting the needs of the Defence Services.

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