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[redacted] 25X1

September 4, 1958

[redacted] 25X1

EXPLANATION RE PATENT AND ROYALTY REPORT

Dear Sir:

In our recent conversations, you requested an explanation of the comments contained in the patent and royalty report dated April 18, 1958, on the patentability of the device conceived under Task Order No. A, Work Order No. IX.

I have talked with our Patent Section on this matter and they indicated that the constant-temperature-environment device conceived was the type of device that could be the subject of a patent. We have no knowledge of an existing device, publication, or patent that would bar the issuance of a patent on such a device. As was indicated in the letter of April 18, no effort has been made from a patent standpoint to uncover such information. Our Patent Section has indicated that it is common practice to survey the patent literature before filing an application, in an effort to determine the novelty of the discovery in question. You may want to have your patent people do this.

If you have any questions with regard to the above, please let us know.

Sincerely, 25X1

[redacted]

[redacted] 25X1

In Duplicate

CONFIDE

~~SECRET~~

Joe

Ralph

CONFIDENTIAL

9 Sept. 58

file: with [redacted] memo under:
Delay Actuator, silicone

25X1

Stating the patentability of any device resulting from a task is routine for all contractors. [redacted] in keeping with their usual methodical handling of all contractual matters, is only stating that to the best of their knowledge — short of making patent literature survey — they believe the constant-temp environment device to be possibly patentable.

25X1

This device is basically a chamber or container which surrounds the unit or item which is to maintained at constant temperature for many hours. It combines the standard vacuum insulation of a "Thermos" bottle with the heat storage capacity of a liquid by using the latent heats of fusion or vaporization. (It is perhaps this latter factor which they feel makes it sufficiently different from the commercial vacuum bottle to warrant its patentability.)

So far we have taken no steps to patent the device. If you would like to know more about the device I believe [illegible]

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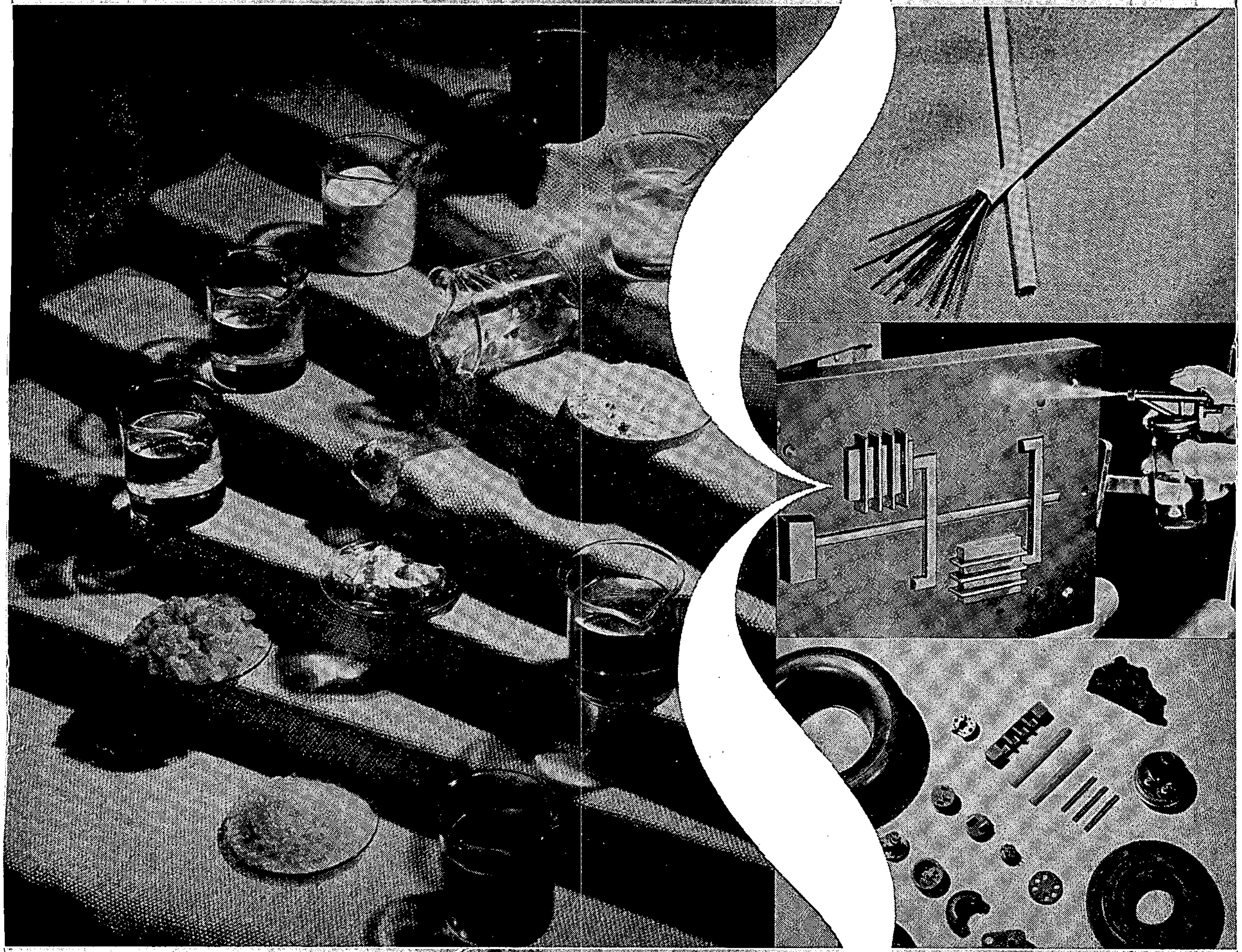
Actuator, Silicone



Silicones

Properties and Uses

by **Kenneth Rose**, *Midwestern Editor, Materials & Methods*

MATERIALS & METHODS MANUAL No. 113

This is another in a series of comprehensive articles on engineering materials and their processing. Each is complete in itself. These special sections provide the reader with useful data on characteristics of materials or fabricated parts and on their processing and applications.

FEBRUARY 1955

In the last decade, a new group of materials has emerged from the laboratories to become part of our everyday lives. They are the silicon-base polymers, and they may be found in a multitude of industrial and consumer products ranging from aircraft gaskets to auto polishes. This manual describes the significant properties and the most important current applications of the "silicones", including—

- ▪ Silicone Fluids and Compounds
- ▪ Silicone Resins
- ▪ Silicone Rubbers

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SILICONES—WAR BABY THAT GREW

The element carbon has always been unique in chemistry in that it has been possible to build from it an infinite number of compounds by substitution and joining reactions. The chemistry of the complex carbon compounds is called *organic chemistry.* Recent developments now make it possible to duplicate this chemistry to some extent with the element silicon which, like carbon, is tetravalent. Polymerized compounds of some complexity, based upon a silicon-oxygen linkage, have been developed, and these organosilicon compounds are known as *silicones.*

Although the chemistry of organosilicon compounds is more than a hundred years old, the production of commercial silicones only began during World War II with the formation of the Dow Corning Corp. as a jointly owned operation of Dow Chemical Co. and Corning Glass Works in 1943. All production at that time was channeled into military uses, but at the end of the war fluid silicones became generally available to industry. By 1945, both Dow Corning and General Electric Co. announced the development of silicone rubbers, and in the following year General Electric opened its own silicone-producing plant. In 1949, Plaskon, then a division of Libby-Owens-Ford Glass Co., started to use silicone-alkyd resins in paints. About that same time, Linde Air Products Co., a division of Union Carbide and Carbon Corp., began pilot plant production of silicones. Dow Corning, General Electric and Linde Air Products are the three producers of primary silicones in the United States today.

■ THE TERM "SILICONES" is a convenient designation for a diverse group of chemical compounds having a silicon-oxygen linkage somewhat analogous to the carbon linkage in organic compounds. Addition of organic side-chains often produces a material that is actually more organic than inorganic. Also, many of the commercial silicones are formulated by mixing them with silica, soaps and other fillers. Thus, the properties of materials called "silicones" may vary over a wide range. In general, however, silicones are chosen for their:

1. Resistance to deterioration at elevated temperatures. Many types can withstand temperatures of 500 F or higher for prolonged periods with little loss of important properties.

2. Maintenance of properties at low temperatures. Silicone resins and rubbers retain flexibility at low temperatures that cause other resins and rubbers to become brittle and useless. Silicone fluids show little change in viscosity in going from ordinary temperatures to low temperatures.

3. Long life. Silicones not only stand up better than organic materials under extreme temperatures, but also last longer than organic materials at intermediate temperatures.

4. Chemical inertness. Incompatibility with many chemicals is important in mold release applications, defoaming, etc.

5. Excellent resistance to deterioration during prolonged outdoor exposure. Resistance to the effects of sunlight and oxidation

TYPES OF SILICONES

Type	Forms	Significant Properties	Major Current Applications
FLUIDS ("oils")	Pure liquid or water emulsion.	Wide range of viscosities, good heat stability, high flash points, low volatility, low freezing points, good dielectric properties, wide useful temperature ranges, good water repellency, chemical inertness.	Damping fluids, hydraulic fluids, dielectric fluids, water-repellents, mold release agents, lubricants, antifoam agents, polishes or cleaners, immersion baths.
COMPOUNDS ("greases")	Fluid thickened with filler.	Same as above. Do not soften and flow readily at elevated temperatures.	Lubricants, sealants, packing impregnations, vibration dampers, mold release agents, antifoam agents, rust preventives.
RESINS	Solid in solvent solution or sometimes in water emulsion. Formulated (often with fillers and/or organic materials) for molding, laminating, coating or foaming.	Good heat stability, good dielectric properties, good water repellency, chemical inertness, good resistance to weathering and ozone.	Molded parts, electrical insulation impregnations, electrical insulating laminates, water-repellents, heat- and chemical-resistant coatings, mold release agents, foamed core structures.
RUBBERS	Solid gums, or compounds containing fillers, vulcanizing agents and additives. Rubber compounds may be (1) solid and formulated for molding, extruding, calendering or sponging, (2) in form of paste, or (3) in solvent dispersion. Also plain or reinforced sheet, tubing and extruded shapes.	Retention of useful strength and flexibility over long period at high and low temperature extremes, chemical inertness, relatively good oil resistance, good dielectric properties, good resistance to weathering and ozone.	Gaskets, electrical insulation. Fabric coatings and impregnations for both electrical and mechanical applications, including gaskets, mats, belting, hose, sleeving, diaphragms. Sealing, calking and potting compounds.

is important in paints, insulation on electric wire, etc.

6. Good water repellency. Silicone fluids and resins are used on both organic and inorganic materials where water repellency is desired. Water repellency is also important in connection with other properties such as dielectric strength.

Of even greater importance than any single property is the unique combination of properties. No other fluids have the combination of good oxidation resistance, low vapor pressure, low freezing point, good heat stability and flat viscosity curve that makes silicone fluids outstanding for aircraft instruments. No other resins or rubbers have the combination of good dielectric strength, good arc resistance, good heat stability, outstanding resistance to ozone and weathering, and good low temperature properties that make silicone resins and rubbers excellent insulation for electrical conductors.

Principal disadvantages of the silicones are high cost, incompatibility with many other substances, some processing difficulties and, in the rubbers, relatively poor strength and extensibility. Also, silicones will burn, and they are adversely affected by many petroleum compounds, particularly the aromatic hydrocarbons used in aviation fuel. Resistance to straight-chain hydrocarbon oils is good, however.

Chemical classification of the silicones is difficult. In this article chemical nomenclature has been largely omitted, and the silicones have been somewhat arbitrarily classified according to their physical state. Hence, five groups are distinguished: fluids, greases and other compounds, resins, rubbers, and specialties. Such a classification is common in the industry and provides a fairly convenient basis for considering specific applications.

Silicone Fluids and Compounds

The silicone fluids or "oils" are clear liquids having excellent stability at elevated temperatures, low freezing or "pour" points, a wide range of viscosities from about 0.65 to higher than 1,000,000 centistokes, and only small change in viscosity through a wide temperature range. They have an oily feel, but conventional types have little lubricating ability and must be used as lubricants only with caution. They are nontoxic and have little chemical reactivity, yet they are effective as additives even in very small amounts. They are colorless, or nearly so.

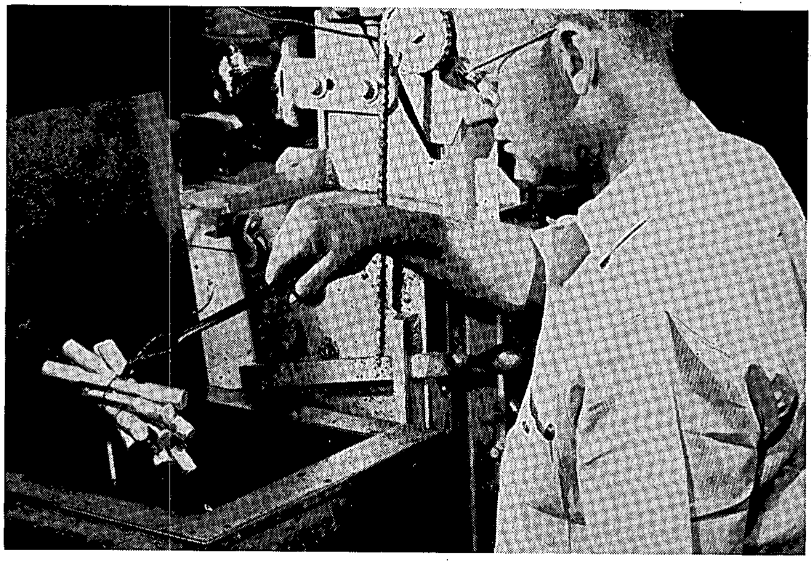
Silicone fluids may be classified in two composition groups: the dimethyl silicones, and silicones other than dimethyl. The first group has two methyl groups for each silicon atom. In the second group some of the methyl radicals are replaced by another organic radical—sometimes ethyl but usually phenyl. The phenyl types are stable at higher temperatures and have slightly better lubricity than the dimethyl silicone fluids.

Silicone fluids are used as bulk fluids, as films, and as additives to other materials. Although high in price, the amount required in many applications is so small that overall cost is often lower than that of less expensive materials. In addition, of course, silicone fluids often make possible economical designs that would otherwise be impossible.

Dimethyl silicones

The dimethyl silicone fluids are known commercially as Dow Corning "200 Fluids", General Electric SF-96 and Viscasil series, and Linde L-series. These materials can be specified by means of the commercial designation, together with the desired viscosity. Significant properties are summarized below:

Heat stability—Stable for long periods at 300 F if in contact



Hot immersion bath *for accelerated aging tests on magnesium at Dow Chemical Co. utilizes high-phenyl silicone fluid. The silicone bath has operated continuously for three years and has provided a net saving, since the previous inexpensive hydrocarbon oil bath had to be replaced each month.* *(Dow Corning Corp.)*

with air, and at 400 F if protected from air. At 475 F in air, viscosity shows considerable increase within 12 hr, and fluid is converted into, or coated with, tough rubbery gel within 48 hr (addition of antioxidant retards gel formation). Heat in the absence of oxygen breaks down fluid into polymers of lower molecular weight (slowly at 475 F, and rapidly above 650 F).

Boiling point—Lowest viscosity fluids boil in the 275 to 350 F range. Fluids with viscosity above 50 cs. are practically unboilable even at reduced pressures. Heated strongly long enough they decompose without boiling, but the lower-viscosity decomposition products may boil.

Freezing ("pour") point—Most dimethyl silicone fluids retain useful fluidity at temperatures no lower than -40 F, but some low-viscosity fluids are useful at temperatures of -100 F and lower.

Viscosity-temperature—Change in viscosity over wide temperature range is much less than for petroleum oils. For example, over the temperature range from -50 to 300 F, the viscosity of a 100-cs. fluid varies from 1000 to 25 cs. The change is small enough so that the normal viscosity index is not applicable and a new viscosity-temperature coefficient has been established.

Viscosity breakdown—Good resistance to viscosity breakdown during prolonged exposure to elevated temperatures. No measurable shear breakdown in fluids having viscosity less than about 1000 cs. Higher-viscosity fluids show small drop in viscosity under shear, but original viscosity is reestablished when shear ceases. Maximum of 10% drop in viscosity reported for 16-hr exposure.

Water resistance—Insoluble in water but not impermeable to water vapor.

Solvent resistance—Insoluble in vegetable oils. Low viscosity fluids are somewhat more soluble in other organic solvents than higher viscosity fluids. See accompanying list.

USES OF DIMETHYL SILICONE FLUIDS

DAMPING FLUID. High-viscosity fluid, together with flywheel mechanism, absorbs torsional vibration energy of crank in diesel and automotive engines. Drop of high-viscosity fluid on pivot or spindle bearings minimizes flutter of indicating needle in automotive and aircraft instruments.

HYDRAULIC FLUID subject to considerable temperature fluctuations, as in aircraft instruments and controls. Such applications have been limited because of certain lubrication difficulties encountered in conventional designs and because of incompatibility of the fluid with rubber seals. However, special rubber compounds have been developed for gaskets in prolonged contact with silicone fluids.

DIELECTRIC FLUID for transformers. Relatively noninflammable fluid with low vapor pressure makes it unnecessary to keep transformers outdoors for safety.

WATER-REPELLENT FILM for wood, rubber, glass, ceramics, and other solid surfaces. One familiar method of application: impregnated paper or "lens tissue" for cleaning spectacles. However, a much higher degree of water repellency is provided by silicone *resins*. Fluids also blended or compounded with organic resin in water-repellent film for fabrics or leather. Silicone-modified organic resin, when cured, imparts smooth, resilient "hand" to fabrics and increases their tear and abrasion resistance.

MOLD RELEASE AGENT applied by wiping or spraying. Widely used for long-lasting release film on automotive tire molds. Also used for glass molding, plastics molding, shell molding and die casting, especially of zinc parts that are not to be painted. Often applied most economically as water emulsion. Silicone fluids eliminate smoke and fumes resulting from carbonization of older petroleum-type parting agents.

LUBRICANT for plastics and sometimes rubber parts. Lubricant for metals where rolling friction is involved. Lubricant for certain metallic combinations where sliding friction is involved. Light to moderate loads only. Example: parking meters. Also used for impregnation of porous bronze bearings. Cutting fluid for machining plastics.

ANTIFOAM AGENT in processing of petroleum oils, tars, hydraulic fluids, syrups, latex coatings, paper pulp slurries and adhesives. Often used in automotive crankcase oil to reduce foaming caused by other common additives. Not applicable to solvents for silicones. Some silicone antifoam agents contain a few percent of a specially purified fine silica.

LUBRICATING FILM ON GLASS. Reduces self-abrasion of woven or unwoven fibers so cloth or mat can withstand repeated flattening without destruction. On glass bottles, inside coating reduces cracking due to impacts during filling and allows contents to be released more readily. Outside coating reduces scratching caused by contact with other bottles. Glass bottle coatings applied simultaneously by vaporizing fluid in oven.

ADDITIVE FOR RUBBER. Incorporated by special techniques into rubber, especially butadiene-styrene and chloroprene synthetics, silicone fluid improves abrasion resistance, weather resistance and stability at slightly elevated temperatures.

POLISH OR CLEANER for automobiles, furniture, windows. Often combined with waxes.

ADDITIVE FOR PAINT in amounts of about 0.2%. Reduces pigment-floating tendency, aids gloss retention, acts as antiflooding agent, and reduces orange peel.

SPRINGS that utilize the compressibility of silicone fluids.

SOME SOLVENTS FOR SILICONE FLUIDS

- Amyl acetate
- Benzene
- Carbon tetrachloride
- Chloroform
- Cyclohexane
- Ethylene dichloride
- Gasoline
- Hexyl ether
- Kerosene
- Methylene chloride
- Mineral spirits
- Naphtha
- Toluene
- Trichloroethylene
- Turpentine
- Xylene

PARTIAL SOLVENTS*

- Acetone
- Butyl alcohol
- Dioxane
- Ethyl alcohol
- Isopropyl alcohol
- Orthodichlorobenzene

* *Partial solvents only for silicone oils having viscosity in 10-50 centipoises range.*

Chemical resistance—Generally inert to dilute aqueous solutions of acids and alkalies, paraffin hydrocarbons. Strong reagents such as solid ferric or aluminum chloride cause increase in viscosity and finally gel formation. Slowly destroyed by concentrated sulfuric or phosphoric acid. Slowly oxidized by concentrated nitric acid at elevated temperatures. Decomposed by gaseous hydrochloric acid or chlorine.

Effect on materials—Do not react with plastics, lacquers and other organic coatings. Fluids of low viscosity and low molecular weight are reported to cause slight leaching of plasticizer and some shrinkage in rubber subjected to prolonged immersion. Noncorrosive to metals. Prolonged contact with steel, aluminum, tin zinc, cadmium or silver has no effect on fluids. Prolonged contact with lead or tellurium at 400 F seems to increase viscosity, and prolonged contact with copper or selenium seems to decrease viscosity slightly.

Flammability—Can be ignited, but will not support combustion alone.

Dielectric properties — Vary with viscosity. Dielectric constant varies from about 2.2 to 2.8, and is little affected by change in temperature or frequency. Power factor, also little affected by temperature, remains low for frequencies up to 100 mc., then rises sharply. Volume resistivity is approximately 10^{14} ohm-cm, and is nearly constant up to about 400 F. Dielectric strength at 10 mils has been reported as 250 to 300 v per mil, and at 100 mils on the order of 500 v per mil. However, values as high as 35 to 40 kv have also been reported for thoroughly-dried fluids at a 100-mil gap.

Lubricating properties—Good for rolling friction. For sliding friction, lubricating ability of dimethyl fluids varies widely wth materials involved. Generally not suitable for steel on steel, though some light-load applications have been successful. Not suitable for steel shaft in graphite bearing. Apparently satisfactory for zinc-plated, chromium-plated, bronze or cadmium-plated (at light loads) shaft in steel bearing and for steel shaft in babbitt, silver or nylon bearing. Also suitable for plastics and rubber bearing combinations.

Compressibility—Low-viscosity fluids more compressible than mineral oils, glycerin and similar fluids. Compressibility decreases with increase in viscosity.

Other silicone fluids

The most important advantages of phenyl-containing or diethyl silicone fluids, compared to the more common dimethyl fluids, are greater heat stability and a broader useful temperature range. Some of these fluids have a freezing or "pour" point as low as -95 F combined with a flash point of 550 F. As the accom-

COMPRESSIBILITY OF SILICONE FLUIDS

Type of Fluid (Kinematic Viscosity, cs.)	Compressibility			
	Under 7100 psi	Under 35,000 psi	Under 284,000 psi	Under 568,000 psi
0.65	6.3	16.3	Freezes	—
2.0	4.9	14.3	31.5	36.9
100	4.5	12.7	28.6	34.0
1000	4.6	12.7	28.2	33.5

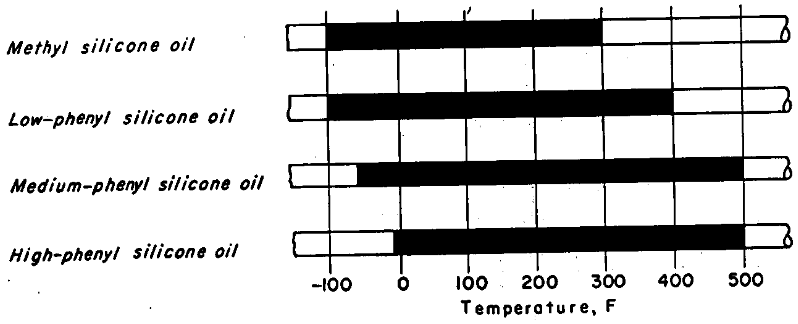
USES OF OTHER SILICONE FLUIDS

HOT IMMERSION BATH. Examples: sterilizing fluid for dental instruments that does not cause rusting and does not smoke when hot; laboratory constant temperature bath; calibration bath. A similar use: heat exchange fluid.

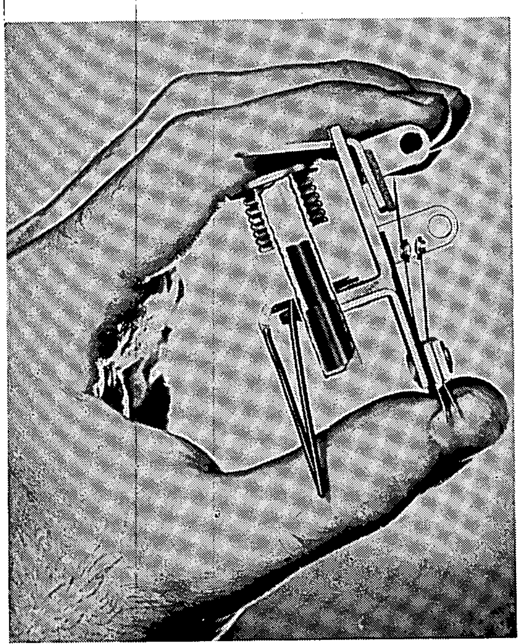
LUBRICANT FOR METALS over wider temperature range than possible with dimethtyl silicone fluids. Suitable for rolling friction and, for certain metallic combinations, sliding friction. Light loads only. Examples: permanent lubrication of electric clocks, electric razors, scientific equipment. One new fluid appears suitable for steel-on-steel sliding friction applications, heretofore not possible with silicones.

WATER-REPELLENT FILM FOR FABRICS. Fluid and resin combined in coating material that must be set with heat—a few minutes at 300 F or less than a minute at higher temperatures. Used for fabrics; also for paper used for protection or interleaving of asphalt packaging, pressure-sensitive tapes, partially cured rubber, etc.

DIFFUSION PUMP FLUID.



Useful temperature ranges for silicone fluids. *(Dow Corning Corp.)*



Relay *made by Heinemann Electric Co. utilizes silicone fluid as damping medium.* *(General Electric Co.)*

panying chart indicates, many are suitable for continuous use at temperatures up to 500 F. Some can be used at higher temperatures for short periods or where a brief service life is acceptable. For example, high-phenyl fluids have been used at 700 F where relubrication of bearings was possible. Addition of an antioxidant increases service life, although the antioxidant itself is eventually destroyed at high temperatures.

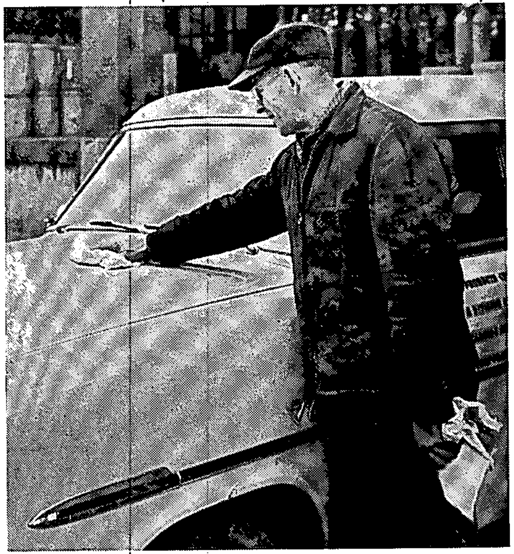
Variation of viscosity with temperature is generally greater in phenyl-containing fluids, particularly in the high-phenyl fluids, than in the dimethyl fluids, but this variation is never as large as in petroleum oils. Phenyl-containing fluids are also much more compatible with organic materials than are dimethyl fluids and, consequently, are not nearly so suitable as mold release agents or as lubricants for plastics. They are also less useful as polishes.

Because of the greater heat stability and broader useful temperature range, phenyl-containing fluids are sometimes preferred to dimethyl fluids as lubricants despite a steeper temperature-viscosity curve. In addition, a phenyl-containing fluid recently announced appears to be suitable for the common lubrication problem of steel-on-steel sliding friction, a type of application for which neither dimethyl nor phenyl-containing silicone fluids have previously been satisfactory. The new fluid is reported to have a useful temperature range from -100 to 500 F and a flatter viscosity curve than most phenyl-containing fluids. It can also be compounded as a grease.

Silicone compounds

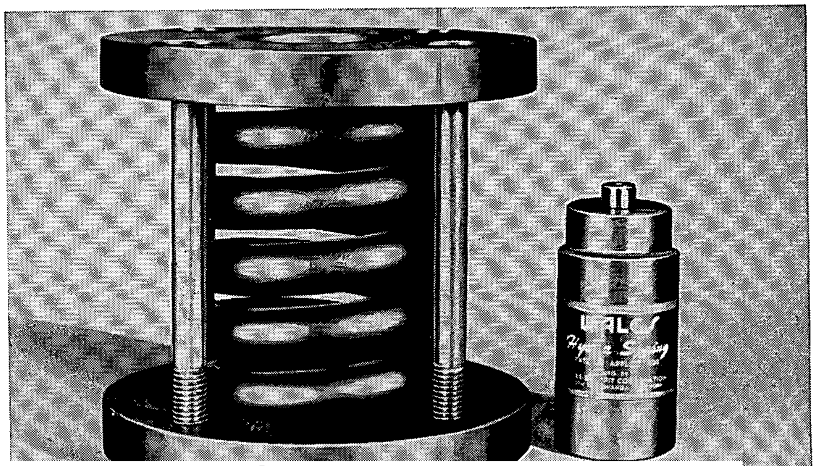
Silicone compounds or "greases" are made by thickening silicone fluids by means of small filler additions. Common fillers are specially purified fine synthetic silica, natural silicates in the form of diatomaceous earth, lithium soap and carbon black. Both dimethyl and phenyl-containing fluids are used in compounds.

Useful temperature ranges for silicone compounds are similar to those for the corresponding silicone fluids. Compounds differ from the fluids in that they can be made so that they do not flow readily at temperatures up to 375-400 F. Like the fluids, they have good dielectric strength, low volatility, chemical inertness, and surface properties useful in lubrication and defoaming.



Car polish *is one of many products that have been improved by silicone fluids.* *(Linde Air Products Co.)*

Springs *utilizing silicone fluids were developed by the Hydra Spring Div. of Wales-Strippit Corp. for use in heavy-duty punches and machine tools. They have almost 10% compressibility at 20,000 psi, and about the same capacity as a conventional spring 12 times as large and five times as heavy.* *(Dow Corning Corp.)*



USES OF SILICONE COMPOUNDS (Greases)

LUBRICANT. Dimethyl types used especially for intermittent motion in high-temperature steam or corrosive environments. Examples: pipe line valves, stopcocks.

LUBRICANT FOR METALS. Low-phenyl and some dimethyl types used especially in low temperature environments, also over broad temperature ranges and at high temperatures. Examples: motor bearings, ball bearings carrying light to moderate loads, time clocks, radar tuning devices, electricity meters and microphone switches.

LUBRICANT FOR METALS. Medium-phenyl types suitable for especially wide variety of uses, including high temperature-high speed applications, contact with corrosive liquids or atmospheres.

LUBRICANT FOR METALS. High-phenyl types, compounded with carbon black, particularly suitable for high temperature-low speed applications. Can withstand 500 F continuously, up to 1000 F for short periods. Examples: bearings in furnace cars, oven doors and oven conveyors.

SEALANT for spark plugs, switches, terminals and other electrical connections in high-flying military aircraft, X-ray equipment, etc. Prevents moisture absorption, corrosion, corona discharge. Also sealant for vacuum and distillation equipment.

PACKING IMPREGNATION to lengthen life of packing in pumps handling corrosive chemicals.

VIBRATION DAMPER. Example: phonograph pick-up.

MOLD RELEASE AGENT Even though more costly, compound sometimes preferred to fluid. Similar uses: prevents glue and resin from sticking to press platens in manufacture of plywood; prevents plastics packaging film from sticking to heating irons or heat-sealing equipment.

ANTIFOAM AGENT used in bottling soft drinks and chemicals, cooking varnishes, concentrating sugar, loading tank cars with latex or tar, etc.

RUST PREVENTIVE. New compound designed for protection of ferrous artillery components during long storage is expected to be useful for delicate instruments that might be adversely affected by ordinary rust preventives.

LUBRICANT FOR RUBBER. New compound has been developed for automotive door weatherstrips, hood bumpers and other parts made of rubber.

Silicone Resins

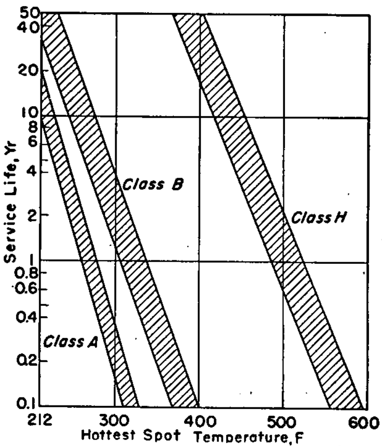
Silicone resins make the unique combination of properties characteristic of the silicone family available to the broad field known as "plastics." What is more important thus far, silicone resins, along with the commercial development of glass fibers and fabrics, have made possible the advent of Class H electrical insulation, capable of long life at continuous operating temperatures much higher than are possible with Class A or B insulation.

The most important properties of silicone resins are good heat stability, good dielectric properties, good water repellancy, chemical inertness and good resistance to weathering and ozone. Since the resins are often filled, reinforced, blended or combined with other materials, the properties of structures made from silicone resins may depend a great deal on the properties of the other materials and on their compatibility with the silicone resins.

Generally, silicone resins can be classified as molding resins, laminating resins, coating resins and foaming resins. The resins themselves are ordinarily supplied as solvent solutions or water emulsions. Like the silicone fluids and compounds, they are high in cost and are used only for special applications not otherwise feasible or where improvement in performance is sufficient to justify the additional materials cost.

Molding resins

Most thermosetting organic moldings, such as the phenolics, are not suitable for continuous exposure to temperatures much above 300 F. Silicone moldings, therefore, are used primarily in the 300-500 F temperature range that is out of reach for the organics.



Life expectancy of Class A, B and H (silicones) insulation for various "hottest spot" temperatures.

(Dow Corning Corp.)

A silicone molding compound is usually made by mixing filler with a toluene or xylene solution of the silicone resin, flashing off the solvent under a partial vacuum, drying the mixture (about 10 min at 225 F) and breaking it up. Fillers are always used. Because most applications involve high temperatures, fillers are limited to heat-stable materials such as silica, glass, asbestos and mica. Of these, glass is most common.

At present, the cost of a silicone molding may vary considerably depending on the source of materials. Some compounds require extremely long post-cures for optimum properties. A post-cure cycle for such compounds is given in the accompanying box which outlines a typical molding cycle. Other new compounds, however, require only a 2-hr post-cure at 300-400 F for optimum properties and are usually not post-cured at all unless a high heat distortion temperature is needed. Such compounds, with molding cycles approaching those for phenolics, seem likely to broaden the industrial applications for silicone moldings.

TYPICAL MOLDING CYCLE FOR GLASS-FILLED SILICONE RESIN

Molding temp	300-350 F
Molding pressure	1000-15,000
Curing time in mold	10-30 min
Mold shrinkage	0.1-0.8%
Postcure (oven)	16 hr at 200 F 2 hr at 260 F 2 hr at 300 F 2 hr at 350 F 2 hr at 400 F
Cure shrinkage	0.1%

TYPICAL PROPERTIES OF GLASS-FILLED SILICONE MOLDINGS

Specific Gravity	1.7-2.0
Tensile Strength	2000-6000 psi
Water Absorp, 24 hr	0.2-0.9%
Max Temp for Continuous Exposure	450-570
Heat Distortion Temp	500-930 F
Dielectric Strength at 60 cycles/sec	100-300 volts/mil
Dielectric Constant:	
60 cycles/sec	3.2-5.0
1 megacycle/sec	3.2-5.0
Power Factor:	
60 cycles/sec	0.002-0.007
1 megacycle/sec	0.002-0.007
Volume Resistivity	10^{13} ohm-cm

Typical properties of a glass-filled silicone molding are shown in the accompanying table.

Laminating resins

Silicone laminates cost more than organic thermosetting laminates, and they are not as strong as the organic laminates at ordinary temperatures. However, the strength of most organic laminates drops off rapidly above 300 F, whereas silicone laminates retain most of their strength at temperatures up to 500 F and above.

Like silicone moldings, therefore, silicone laminates are confined primarily to applications involving continuous exposure to temperatures in the 300-500 F range or brief exposures to higher temperatures. They are widely used for Class H electrical insulation. Glass cloth is the most common reinforcement, although asbestos and mica are also used.

Silicone laminates and molded laminates are made by procedures similar to those used for organic laminates. Typical laminating procedures and some properties of a typical laminate are given in accompanying boxes.

One peculiar advantage of silicone laminates as electrical insulation in certain applications is the electrically insulating ash that remains even when the insulation has been completely burned. For example, the Navy found that armored cable might continue to function after a severe local fire, thus allowing a ship to return to base for repairs under its own power.

TYPICAL PROPERTIES OF CURED SILICONE-GLASS LAMINATES

Tensile strength	35-45,000 psi
Water absorp, 24 hr	0.05-0.7%
Dielectric str, ⅛ in.	360-420 v/mil
Power factor, 100 mc	0.003

Coating resins

Silicone and modified silicone resins are widely used in paints, as nonadhesive films, and as water-repellent films.

Silicone coatings alone are serviceable at temperatures up to about 500 F. Aluminum-pigmented modified-silicone coatings can be used at 1000 F and for short periods as high as 1500 F. At such temperatures, the silicone film no longer exists as such but the pigmented paint continues to provide protection against oxidation.

In "modified" paints, silicone resins are combined with organic resins, primarily alkyd resins. The resins may be combined merely by blending or by copolymerization. Silicone additions, generally of 25% or more, improve the heat stability, gloss retention, non-yellowing properties and water repellency of conventional alkyd paints. Even a 5-10% addition improves weather resistance. Silicone-alkyd paints have top service temperatures about

TYPICAL LAMINATING PROCEDURE FOR SILICONE-GLASS CLOTH

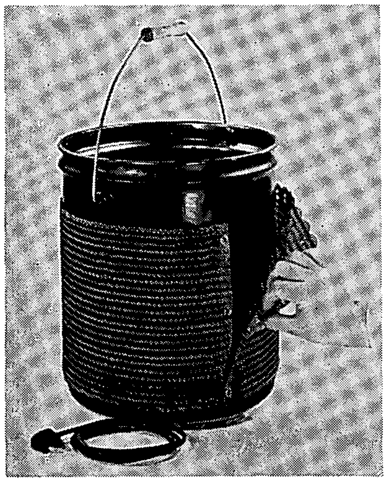
1. Remove any organic sizing from glass cloth by heat-cleaning.
2. Immerse cloth in solvent solution of silicone laminating resin.
3. Air-dry impregnated cloth about 30 min.
4. Further dry impregnated cloth 5-10 min at about 225 F.
5. Lay up (or wind) impregnated sheets to form sheet, rod, tube, moldings, etc.

HIGH-PRESSURE:

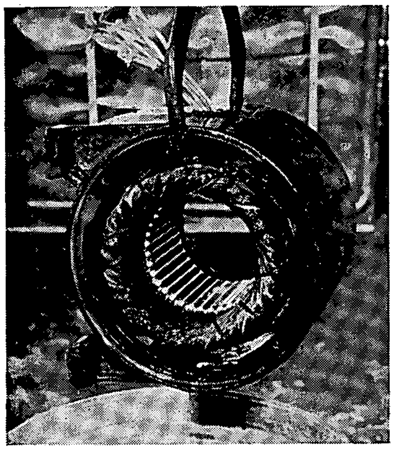
6. Cure laminate 1¼ hr at 350 F under 900 psi, and cool 30 min under pressure.
7. Heat 15 hr at 200 F.
8. Raise temperature to 375 F through 8 hr, and heat 16 hr at 375 F.
9. Heat 4 hr at 480 F, and cool.

LOW-PRESSURE:

6. Cure laminate at 350 F under contact pressure for 15-60 min, depending on section thickness, and cool.
7. Heat 16 hr at 200 F.
8. Raise temperature to 480 F through 4 hr, and heat 80-150 hr at 480 F.



Net contact heater *made by Pre-Fab Co. for melting 5-gal drums of plastisol has nylon-reinforced glass cord insulation impregnated with silicone resin varnish. Device was originally developed to keep high altitude aerial cameras and control mechanisms operative in sub-zero environments.* (Dow Corning Corp.)



Electric motor *emerges from dip tank en route to baking oven where silicone resin varnish will be cured. Overall silicone coating is final step in rewinding motor with Class H insulation.* (Linde Air Products Co.)

100 F lower than those for silicone films alone. However, the modified silicone films are more easily applied and quicker drying than the straight silicones.

Silicone and modified silicone paints are applied preferably by spraying. Roller coating and especially brushing are not generally recommended. Optimum properties are obtained by an elevated temperature cure. Straight silicone coatings may

USES OF SILICONE RESINS

HEAT-RESISTANT LAMINATE, primarily for use in the 300-500 F range. Especially Class H insulation. Examples: spacers and barrier sheets in dry transformers, and slot wedges, spacers and other mechanical supports in electric motors. Silicone laminates of glass, asbestos or a mica-glass cloth sandwich increase permissible operating temperatures and thereby make possible smaller, lighter transformers and motors for given output. It has been estimated that although a silicone-insulated motor costs about 75% more than a Class A or B motor of the same size, its cost based on dollars per horsepower output is about the same or sometimes less.

SILICONE PAINT OR VARNISH. Varnish used especially on electric motors, circuit chassis. Aluminum-pigmented modified-silicone paints especially suitable for use in the 300-500 F range and for brief exposures to temperatures as high as 1500 F. Examples: Stacks, stack breeching, stoves and furnaces, steam pipes, exhaust lines and sterilizing racks. Such paints often cured in service. Other types used for automobile manifolds, vehicle heaters, non-yellowing white finish for hospital equipment. Modified-silicone enamel also used as wire insulation. Results of one series of tests indicated that induction motors wound with silicone-coated wire and operating at 325-360 F had the same life expectancy as similar motors wound with Class A insulation and operating at about 190 F.

HEAT-RESISTANT MOLDING utilizing glass, asbestos or diatomaceous earth filler. Examples: switch parts, brush ring holders in electric motors, coil forms.

FOAMED LOW-DENSITY STRUCTURE made by shaping prefoamed block or sheet or by foaming resin in place. Expected applications: cores in high-speed aircraft structures and thermal insulation for other high-temperature structures.

MOLD RELEASE AGENT applied as emulsion or solvent solution. Especially effective with metal patterns in shell molding process. Another example: silicone resin coating on bakery pans lasts for weeks, eliminating cost of material and labor required to grease pan before each bake and providing net saving despite hundred-fold higher initial cost. Also makes release of baked goods from pan much easier.

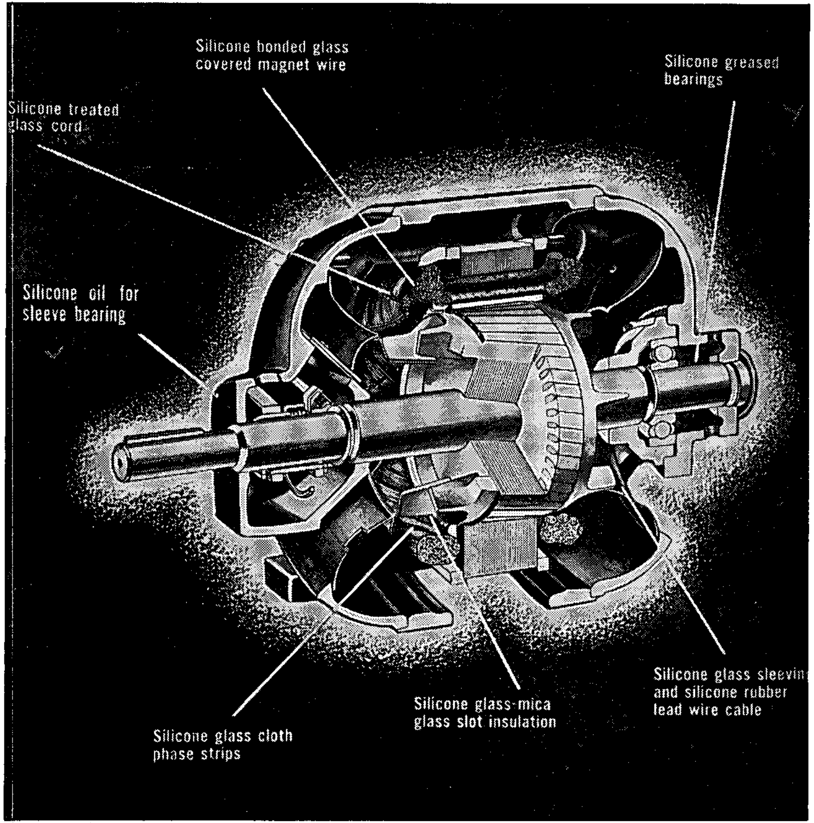
WATER-REPELLENT COATING for masonry and concrete. Provides invisible film that is permeable to water vapor and thus reduces condensation of moisture inside walls.

WETTING AGENT. Examples: Coating for alumina grits to improve bonding in resin-bonded grinding wheels. Sizing for glass cloth to improve adhesion to polyester resins in low-pressure laminates.

SPECIAL APPLICATION: chemical-resistant electrical insulation for glass radiant heating panels. Silicone insulation pattern applied to metal surface of aluminum-glass sandwich by silk screen process. Unprotected aluminum etched away by caustic soda leaving silicone-insulated aluminum heating grid.

ADDITIVE FOR PIGMENT to improve dispersion in paints, inks.

INGREDIENT OF HEAT-STABLE MOLDING COMPOUND based on organic resin. Now under development.



Electric motor—*How silicone fluids, greases, resins and rubbers increase its efficiency.* *(General Electric Co.)*

be cured in about 1 hr at 480 F or 4 hr at 400 F. Lower temperatures can be used for the modified silicones. Silicone and modified silicone paints are often cured automatically in service.

Silicone resin release films may be applied from either solvent solution or water emulsion and cured by baking. They are used for semi-permanent release applications, as on bakery pans.

Resin solutions or emulsions for water repellency applications contain about 5% or less solids as applied and are used on non-flexible surfaces. Films for masonry and concrete generally cure at ordinary temperatures.

Foaming resins

Foamable silicone resins, analogous to the foamable organic resins, are available for the production of low-density parts. Some of these silicone resins can be foamed in place and can therefore be used to form low-density cores in relatively inaccessible cavities. Other resins cannot be foamed in place but can be used to make prefoamed blocks and sheets which can be formed with woodworking tools. Both types of silicone foams are produced by application of heat at temperatures in the 260-360 F range.

Foamed silicone structures can be produced in densities ranging from 6 to 24 lb per cu ft. They are reported to show virtually no dimensional change after 20 hr exposure at 700 F, and less than 2% weight loss after 220 hr at 570 F. Prefoamed structures generally have somewhat better strength than foamed-in-place structures at elevated temperatures. However, foamed-in-place structures made from one resin retain good compressive strength at temperatures as high as 500-600 F. Moisture absorption of foamed structures after exposure in air at 96% relative humidity for 7 days has been reported as less than 0.05%. Foamed silicones are nonflammable.

For some time, silicone resin formulations for foaming in place were available only as two separate components that had to be mixed properly at time of use. Recently, however, a premixed powder has been made available. Shapes made from one of these resins can be postformed considerably when heated to about 200 F.

Silicone Rubbers

Like the other silicones, silicone rubbers have an exceptionally broad useful temperature range compared with organic materials. Silicone rubbers not only supplemented the resins in creating Class H electrical insulation for use at high operating temperatures but, at the other extreme, provided the first practical answer to gasketing problems in high-altitude military aircraft subject to prolonged subzero temperatures. Whereas other heat-resistant synthetic rubbers have poor low temperature properties, silicone rubbers make it possible to obtain good properties at both ends of the temperature scale in a single material.

Properties

The range of properties offered by silicone rubbers is indicated by the accompanying tables adapted from AMS and ASTM specifications. These and other significant properties are summarized briefly below:

Heat stability—Maintain properties indefinitely at about 300 F.

AMS STANDARDS FOR SILICONE RUBBERS[a]

Property[b]	Type	3301B (General purpose)	3302B (General purpose)	3303C (General purpose)	3304B (Low compression set)	3305C (Low compression set)
Hardness, durometer "A"		40 ± 5	50 ± 5	60 ± 5	70 ± 5	80 ± 5
Tensile Strength (min), psi		500	500	400	500	500
Elongation (min), %		250	200	100	60	60
Tear Resistance (min), lb/in.		55	35	35	25	25
Oil Resistance: after 70 hr in ASTM Oil No. 1 at 350 F (ASTM D471-51T)[c]	Change in Durometer "A" Hardness No.	−15 to +5	−15 to +5	−10 to +5	−10 to +5	−10 to +5
	Reduction in Tensile Strength (max), %	50	40	20	20	10
	Reduction in Elongation (max), %	50	20	20	20	10
	Change in Volume, %	0 to +15	0 to +15	0 to +10	0 to +10	0 to +10
Dry Heat Resistance: after 24 hr at 450 F (ASTM D573-48)[d]	Change in Durometer "A" Hardness No.	0 to +10	0 to +10	0 to +10	0 to +10	0 to +10
	Reduction in Tensile Strength (max), %	15	10	10	10	10
	Reduction in Elongation (max), %	25	25	25	25	25
Compression Set: compressed 22 hr at 350 F (ASTM D395-49T, Method B)	Percent of Original Deflection (max)	72[e]	72[f]	60[f]	30[g]	36[g]
	Percent of Original Thickness (max)	29[e]	22[f]	18[f]	8[g]	9[g]
Low Temperature Brittleness (ASTM D736-46T)		Pass 5 hr at −85 F	Pass 5 hr at −85 F	Pass 5 hr at −70 F	Pass 5 hr at −70 F	Pass 5 hr at −70 F

[a] *Adapted from Aeronautical Materials Specifications copyrighted 1952 by Society of Automotive Engineers, Inc.*
[b] *Other requirements: satisfactory resistance to weathering, corrosion.*
[c] *Other requirements: no decomposition, no tackiness.*
[d] *Other requirements: no surface hardening, no cracking or checking when bent flat (90° on 2t radius for 3305C).*
[e, f, g] *Compressed to 60%, 70% and 75% of original thickness, respectively.*

At 400 F, hardness increases gradually and elongation decreases. Tensile strength may drop or increase slightly, depending on the particular material. Changes are rather sharp during first 20 days at temperature, then level off, indicating retention of useful residual properties. At 480 F the same changes occur, but the initial changes are greater. Subjected to excessive heat in air, silicone rubbers become hard and dry and eventually decompose as brittle materials. Heated in the absence of air, however, they become soft.

Low temperature flexibility—Ordinarily retain flexibility down to -70 F, and materials formulated especially for low temperature service can be used at -130 F or slightly below. Since low temperature flexibility is obtained by slight change in basic composition, not by addition of a plasticizer, low-temperature rubbers retain good elevated temperature properties. In ordinary silicone rubbers, hardness starts

ASTM STANDARDS FOR SILICONE RUBBERS[a]

Specification	Grade	TA 505	TA 604	TA 704	TA 805
BASIC REQUIREMENTS					
	Durometer Hardness No.	50 ± 5	60 ± 5	70 ± 5	80 ± 5
	Tensile Strength (min), psi	500	400	400	500
	Ultimate Elongation (min), %	200	100	75	50
Heat aged 70 hr at 450 F	Change in Durometer Hardness No. (max)	+20	+20	+15	+15
	Change in Tensile Strength (max), %	−30	−30	−25	−25
	Change in Ultimate Elongation (max), %	−40	−50	−40	−40
SPECIAL REQUIREMENTS					
Suffix B	Compression set after 70 hr at 300 F (max), %	50[b]	40[b]	40[b]	40[b]
Suffix E_1 (70 hr at 300 F in ASTM Oil No. 1)	Change in Tensile Strength (max), %	−20	−20	−20	−20
	Change in Ultimate Elongation (max), %	−20	−20	−20	−20
	Change in Durometer Hardness No. (max)	−15	−15	−15	−15
	Change in Volume, %	0 to +20	0 to +20	0 to +20	0 to +20
Suffix E_3 (70 hr at 300 F in ASTM Oil No. 3)	Change in Durometer Hardness No. (max)	−30	−35	−40	−45
	Change in Volume, %	+60	+60	+60	+60
Suffix F_2 (5 hr at −65 F)		Pass	Pass	Pass	Pass
Suffix L (168 hr in water at 158 F)	Change in Durometer Hardness No. (max)	−10[c]	−10	−10	−10
	Change in Volume, %	+10[c]	+10	+10	+10

[a] *Adapted from table on "Physical Requirements of Synthetic Rubber Compounds, Type T, Class TA, Temperature Resistant" in ASTM D735-52aT (Rubber and Synthetic Rubber Compounds for Automotive and Aeronautical Applications).*
[b] *Lower values can be obtained with sacrifice of tensile strength and elongation.*
[c] *These values can be met with sacrifice of tensile strength and elongation.*

TYPICAL PROPERTIES OF SILICONE RUBBERS[a]

Property / Type	Low Compression Set (Class 300)	General Purpose (Class 400)	Extreme Low Temp (Class 500)
Hardness, Shore A durometer	50-80	50-90	40-80[b]
Tear strength, lb/in.	30-50	50-75	50-75[b]
Tensile strength, psi	570-750	570-800[c]	700-840[b]
Elongation, %	175-100	370-70[c]	350-90[b]
Compression set after 22 hr at 300 F, %	20-7	50-60	50-80
Brittle temp, (ASTM D 736, 5-hr soak), F	−80 to −65	−90 to −80	below −130 to −120
Stiffness temp, (ASTM D 797, 24-hr soak, modulus = 10,000 psi), F	−50 to −45	−60 to −45	below −120 to −110
Increase in durometer hardness no. after 70 hr at 450 F (heat stability)	6-5	6-3	5-3
Increase in volume after 70 hr in ASTM Oil No. 1 at 300 F (oil resistance), %	8-5	9-6	9-7
Increase in volume after 70 hr in water at 212 F (water absorption), %	high to <1	high to 3	high

(*Courtesy General Electric Co.*)

NOTES:

[a] *Compounds oven cured 24 hr at 480 F except where otherwise noted.*
[b] *Stocks cured 1 hr at 300 F.*
[c] *Properties can be improved with shorter cures where deformation at high temperatures is not factor.*

to increase appreciably at about -20 F and rapidly at about -50 F. As hardness increases, tensile strength increases and elongation decreases correspondingly. In low-temperature rubbers, hardness starts to increase measurably at about -50 F and rapidly at about -100 F.

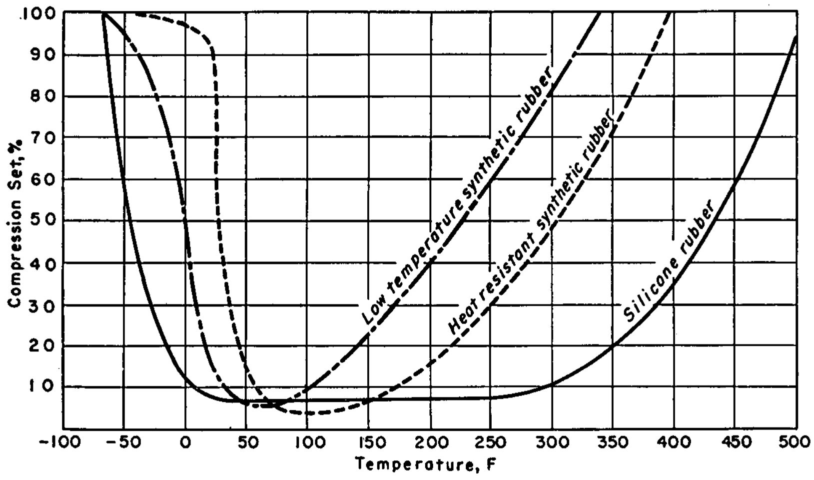
Tensile properties — At room temperature most silicone rubbers are not nearly as strong as natural and other synthetic rubbers. Tensile strength of most stocks falls in the 400-1000 psi range—about one-third the tensile strength of most natural and synthetic rubbers. However, tensile strengths up to 2000 psi are reported for some new compounds. Similarly, ultimate elongation generally ranges from 75 to 600%, but the new high-strength compounds have elongations up to 800%. Tear strength of the new compounds is also improved. In some of the new compounds, higher strengths are achieved at the sacrifice of some heat stability.

Hardness—About 35 to 95 on the Shore durometer "A" scale. Does not increase greatly until very low temperatures are reached, and is relatively constant at elevated temperatures.

Compression set—Compression set of organic rubbers is normally determined at 158 F whereas compression set of silicone rubbers is determined at 302 or 348 F. Hence, results are not strictly comparable. Silicone rubbers have a compression set of about 50%, a figure equivalent to that for heat-resistant organic rubbers. Silicone rubbers with low compression set—as low as 10% — have normally been obtained by incorporating 1 or 2% of mercury or cadmium oxides in the stock. However, a new type of silicone rubber recently announced offers compression set values in the 12-20% range inherent in the gum itself. The new rubber makes possible low compression set without special compounding and also makes low-set materials suitable for use in contact with food and beverages.

Oil resistance—Quite resistant to attack by aliphatic compounds, but swelled by exposure to aromatics. In one series of tests of lubricating oils silicone rubbers and an oil-resistant organic rubber were immersed in a low-swell oil for 72 hr at 350 F. Silicone rubbers retained 83 to 117% of original tensile strength, compared to 67% for the oil-resistant organic rubber, and 93 to 118% of original elongation, compared to 63% for the organic rubber. The silicone rubbers swelled 5 to 8%, and the organic rubber 8%.

Chemical resistance — Resist most alkalies and weak acids, corrosive salt solutions, and oils. Swell in aromatic solvents, gasoline and carbon tetrachloride. Original properties largely regained after removal from unfavorable environment and evaporation of the fluid absorbed by the rubber. Exceptional resistance to ozone, and good resistance to most aromatic chlorinated hydrocarbons (used in liquid transformers), liquid ammonia and Freon 114 refrigerants. Attacked by concentrated acids, methyl chloride and Freon 12.



Compression set of silicone and other synthetic rubbers at temperatures from —70 to 500 F. *(Dow Corning Corp.)*

Dielectric strength—Good and, in the electrical grades, reasonably constant over the temperature range up to 480 F. Since the silicones are ordinarily used fairly thick, the 800 v per mil dielectric strength of many electrical grades is satisfactory for most purposes. Stocks having dielectric strength of 1200 v per mil in low thicknesses are also available. Dielectric constant is about 3.0 to 10.0, depending on the material, and is nearly constant through a wide range of frequencies and temperatures. Power factor ranges from 0.005 to 0.028 for frequencies from 100 to 100,000,000 cycles per sec. Arc resistance is good, since the arc leaves a track of nonconductive inorganic matter instead of a path of carbonized material.

Water absorption—About 1% for most silicone rubbers, but it may be as high as 6% for some rubbers containing hydrophilic fillers.

Steam resistance—Silicone rubber hose generally has not been suitable for handling high-pressure steam, but the new low-compression-set type is reported to have much improved resistance to high-pressure steam.

Abrasion resistance — Low in most silicone rubbers but considered sufficient for most purposes. Likely to be improved with further development.

Compounding

Silicone manufacturers produce both gums and compounds. Gums are the basic silicones which must be compounded to produce commercially usable rubbers. Some fabricators prefer to buy standard compounds, while others prefer to buy the gums and formulate their own compounds.

Silicone rubber compounds consist of the following:

The gum—About six different gums, varying in chemical composition and degree of polymerization, are available.

Fillers, reinforcing agents — Silica is as important to silicone rubber as carbon black is to natural rubber. Usually it is used in the form of a fine synthetic material, but sometimes silicates in the form of diatomaceous earth are used. Manufactured silicas may be alkaline or acid, of many different particle sizes, and of varying degrees of purity. Highest tensile strengths yet reported for silicone rubbers have been obtained with a new synthetic silica filler having exceptionally low particle size.

Although silica is the most important filler for silicone rubbers, other materials are also used:

1. Calcium carbonate. Several types used, especially in coating pastes or adhesives. Not for general molding or extrusion, since tensile strength and elongation of finished stock are usually low.
2. Red iron oxide. Provides good heat aging characteristics and may be used to improve heat stability of stocks containing other fillers. Tensile strength of about 500-700 psi and elongation of about 175-250% may be expected in cured stock for coating pastes.
3. Titania. Provides good heat stability but poor reinforcement and is not much used at present.
4. Zinc oxide. Sometimes used with titania.
5. Alumina. Has produced stocks with high tensile strength and elongation in experimental work.
6. Zirconium silicate. For stocks with high tensile strength but not high heat stability. Stocks with zirconium silicate as the only filler have retained flexibility at 600 F.
7. Clay. Used with other filler such as silica to provide smoother flow in processing, especially in extruded wire insulation where mechanical strength is not important.
8. Carbon black. Sometimes used to provide black color. Has little reinforcing effect and may impair resistance to heat aging.

Vulcanizing agents (catalysts) —Benzoyl peroxide is the most common vulcanizing agent; 2,-4 dichlorobenzoyl peroxide and other peroxides are also used. They are available as powder and as pastes utilizing silicone fluids. Vulcanizing agents are used in amounts from 1 to 3% by weight of the gum. A silicone gum announced recently utilizes sulfur as the vulcanizing agent.

Special additives — Materials such as mercury oxide, cadmium oxide and 2,5 ditertiary butyl quinone are used primarily to improve compression set. Other additives may be used to improve processibility or heat aging characteristics.

Forms and fabrication

Compounded silicone rubbers are available in three different forms: solid compounds, pastes, and dispersions. The form used is determined by the nature of the product and the processing method required.

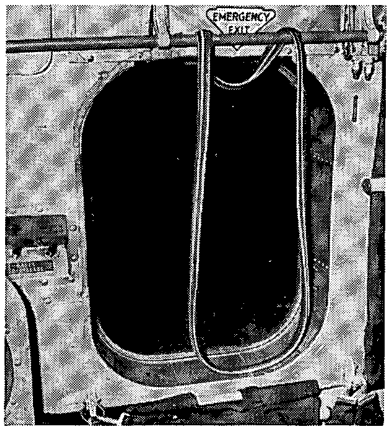
Solid compounds—A great variety of silicone rubber compounds are available, and others may be made from gums to meet special requirements. Solid compounds are processed by molding, extruding, calendering or sponging (when a blowing agent is added). Compounds are often milled for a few minutes prior to fabrication in order to improve processibility.

The complete vulcanization or cure of a silicone rubber is normally accomplished in two steps. The "pre-cure", which results in a certain degree of cross linking, is usually performed under pressure in a mold or in a steam vulcanizer. Some recently developed compounds are pre-cured in hot air without pressure. The final cure, or "post-cure", is done in an oven.

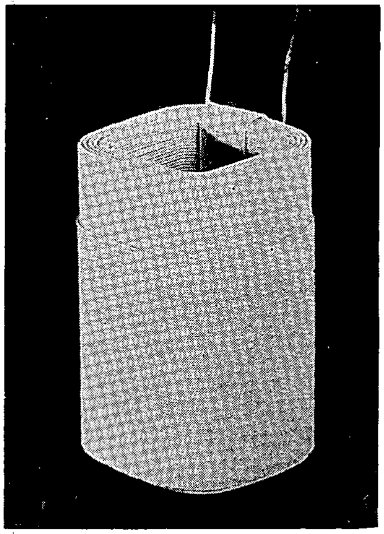
Molding of silicone rubber is done in heated molds at temperatures of 240 to 300 F and mold times of 3 to 20 min. In general, silicone rubber is molded at lower temperatures and shorter times than organic rubbers and, since the mold cure is normally followed by at least a short oven cure, mold time and temperature are not as critical for silicone rubber as for most organic rubbers. Partly because of a higher coefficient of thermal expansion, most silicone rubbers have somewhat higher mold shrinkage than organic rubbers—about 3-4% for silicones compared with about 1.8-2.5% for commonly used synthetic rubbers. The subsequent oven cure increases the total shrinkage of most silicone rubbers to 5-7%. Some new silicone rubber compounds, however, have nearly the same total shrinkage as organic rubbers and can often be fabricated in molds designed for organic rubbers. The inherent nonadhesive characteristics of the silicones make mold release usually simpler for silicone rubbers than for organic rubbers. However, the silicone fluids and compounds most commonly used as release agents for organic rubbers are ineffective for silicone rubber, and dilute solutions of common detergents are ordinarily used.

Extruding of silicone rubber is done at 100 to 125 F. Since the process is exothermic, no outside heat need be added and water-cooling is sometimes necessary. Extrusion stocks are selected or compounded for smooth working in the extruder. The extruded shape is pre-cured in a steam vulcanizer under about 50 psi for about 3-15 min. Some special extrusion stocks (particularly those containing 2,4-dichlorobenzoyl peroxide as the vulcanizing agent) can be pre-cured in hot air without pressure, either in an oven or continuously in a hot air tunnel as the extruded shape emerges from the extruder. In this case, the pre-cure requires only 30-60 sec exposure to air at 600-800 F. Such a quick cure is advantageous in that it prevents collapse of the extrusion, thereby making feasible difficult shapes and closer tolerances.

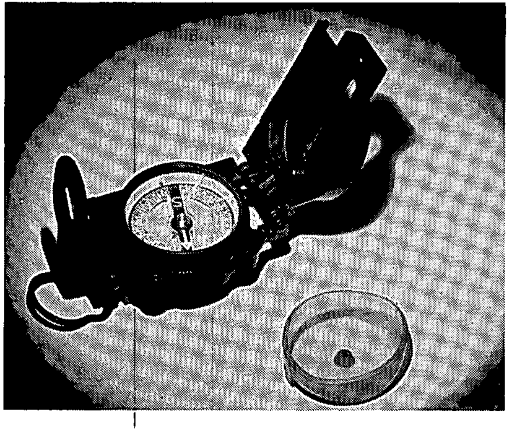
Calendering is normally done on unheated rolls, although the top roll of the three- or four-roll mill is sometimes warmed slightly. Pre-cure of sheet stock is similar to that for extruded stock. Calendering may be used to produce sheet stock or, often, to calender silicone rubber on to supporting fabrics such as glass, Dacron, Orlon or nylon cloth. Asbestos fibers and wire are also used sometimes as supporting materials. The post-cure for supported sheet stock, of course, is



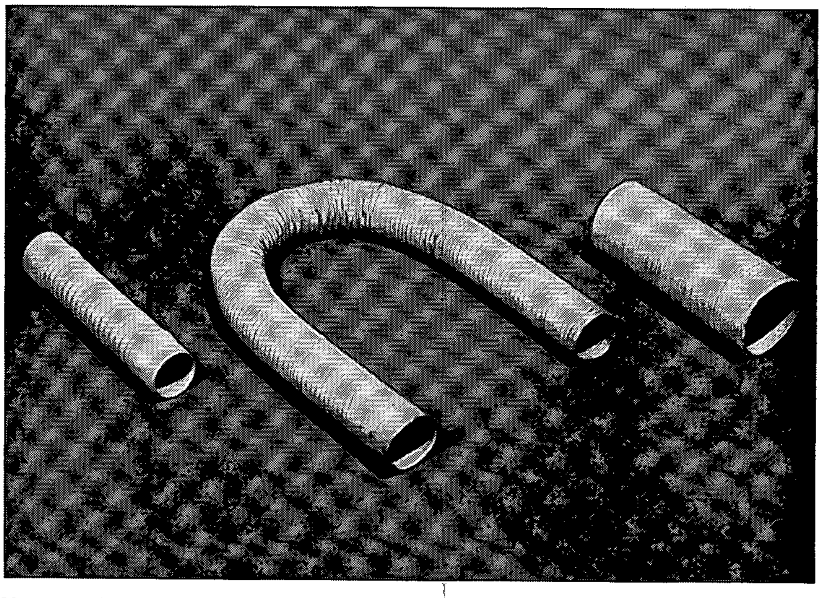
Gaskets *for emergency hatches and other fuselage fittings on Douglas C-124 Globemaster are made of special silicone rubber that remains flexible at temperatures down to —120 F and does not stick to metal after long inactivity.* *(General Electric Co.)*



Coil *subject to operating temperatures as high as 600 F utilizes silicone rubber as encapsulating compound.* *(General Electric Co.)*



Pocket compass *operates over a temperature range of —85 to 160 F, is protected against moisture and shock by silicone rubber molded cup, shown in foreground.* *(General Electric Co.)*



Heater ducts *made of glass cloth coated with silicone rubber.* *(General Electric Co.)*

limited by the heat stability of the supporting material. Calendered stock, both supported and unsupported, may be used in sheet form or formed into hose or tubing by mandrel wrapping.

Sponging of silicone rubber is done by heating a suitable compound which contains a blowing agent. Blowing agents are usually proprietary compounds which produce nitrogen gas upon heating. Sodium bicarbonate, which produces carbon dioxide, is also used.

For some silicone applications no heat treatment of the compound beyond the pre-cure is necessary, but for most applications an additional post-cure in a circulating-air oven is a prerequisite for optimum properties. Essentially, the post-cure eliminates volatile substances, some of which are products of the initial vulcanization reaction and some of which are volatile silicones. Volatile substances must be eliminated to assure stable performance at high temperatures.

The post-curing cycle depends on a number of factors, including the particular compound used, the shape and cross-section of the part, and the expected service conditions. Although few broad rules can be stated, it is generally true that a silicone rubber part should be post-cured at a temperature approximately equal to the highest temperature it will encounter in service. Recommended cure time increases as cure temperature increases, e.g., from possibly 1 hr at 300 F to the commonly-specified 24 hr at 480 F. The longer oven cure normally results in lower compression set and elongation, higher durometer hardness, and better oil and solvent resistance. Other properties, such as tensile strength, vary with the particular compound.

The so-called "full" oven cure of about 24 hr at 480 F is recommended for any part which is expected to be subject to particularly severe deformation, particularly compression, in order to develop maximum resistance to compression set. On the other hand, a part which is to be subjected to negligible stresses at service temperatures even as high as 500 or 600 F can often (depending upon the compound) be used with little or no oven cure, since the post-cure, in effect, occurs in service.

Pastes—Silicone rubber pastes, varying in consistency from soft or salvelike to stiff or puttylike, make possible additional fabrication techniques, as well as certain special applications.

Thin pastes having a Williams plasticity of about 10-40 can be applied directly to fabrics with a doctor blade. When applied to inorganic materials, such as glass cloth, wire cloth or asbestos cloth, the paste is cured for 3-10 min at 400-600 F in an oven or tower. When applied to organic fabrics, such as cotton, nylon, Orlon or Dacron, a lower-temperature cure is used—usually 10-15 min at 260-300 F.

Thicker pastes having a Williams plasticity of about 40-90 are used for sealing or calking and, to some extent, potting. Some of the newer pastes, primarily those filled with calcium carbonate, have appreciably better abrasion resistance than earlier pastes. The heavier pastes are usually cured 15-30 min at 250-275 F.

Pastes may be used to coat metal, glass or ceramic surfaces. Such surfaces require careful precleaning. Solvent degreasing followed by sandblasting or shot blasting is recommended for metals, and increased adhesion is obtained by means of a special silicone primer, especially on copper and copper alloys.

Dispersions—Thick pastes (described above) in the form of solvent dispersions are used to coat fabrics, mats or solid surfaces by dipping, spraying or brushing. The solvent dispersion technique is also replacing the older thin paste technique for knife coating of fabrics because of the superior properties of the resulting coatings.

Solvents used are primarily xylol or toluol. Dispersions for dip coating usually contain about 20-25% solids, and for knife or roller coating about 35-50% solids. Knife or roller coating produce thicker films than dip coating.

After the coating has been applied, the solvent must be driven off and the solid film cured. Evaporation of solvent should take place at a temperature no higher than 170 F and preferably at the

USES OF SILICONE RUBBERS

MOLDINGS, EXTRUSIONS, AND DIE-CUT PARTS. Especially gaskets for bomb-bay doors and other aircraft openings, domestic steam irons, kitchen ranges, autoclaves and pressure cookers, searchlights.

COATED FABRICS. Silicone rubber applied as paste or solvent dispersion to glass, asbestos, wire, cotton, nylon, Orlon or Dacron, and cured. Applications: gaskets, diaphragms, belting, sleeving, hose, tubing, mats, flexible couplings.

LAMINATE OR MOLDED LAMINATE made from fabric bonded to extruded or calendered silicone rubber or silicone sponge rubber, especially for aircraft gaskets and seals.

ELECTRICAL INSULATION for motor lead wires, cables and other external conductors where high operating temperatures, moisture or corona discharge are encountered.

SEALING, CALKING AND POTTING PASTE. Example: embedment of aircraft heating and de-icing elements.

NON-STICK PARTS. Examples: Sleeves for rolls of machines processing pressure-sensitive tape or applying adhesives. Guide wheel handling hot glass sheet and tubing in glass manufacture.

NON-STICK OR WATER-REPELLENT COATING applied as paste on metal, glass or ceramic surface.

VIBRATION DAMPER. Silicone sponge rubber used for shock absorption, vibration dampening and soft low temperature sealing.

COATING FOR ORGANIC RUBBERS to extend useful temperature range, protect against oxidation and corona discharge.

lowest temperature practicable. Incomplete removal of solvent, on the other hand, may result in incomplete vulcanization. Cure time and temperature are interrelated, cure time being shorter at higher temperatures. With an organic fabric base, cure temperature may be limited by the endurance of the fabric. Films up to 5 mils thick may be pre-cured 5-10 min in an air-circulating oven or tower at 250-300 F and post-cured 5-10 min at 400-600 F. Heavier films should be applied as separate coats, and each coat separately and completely cured.

Reclaimed Silicone Rubber—Silicone rubber scraps, trimmings and rejects can be reclaimed and combined with new stock in amounts of 10 to 30%. The lower the degree of cure of the scrap the more readily it can be reclaimed. One method is to merely work the scrap for some time on rolls at about 120-125 F, then mill it together with the virgin rubber. Another method is to grind the scrap to about 5-10 mesh size, autoclave it at 50-100 psi to break some of the chemical bonds, air-dry it, work it on a mill until it is soft, and then mill it together with the virgin rubber. Amounts of about 10-15% of reclaim prepared by this latter method reduce mold shrinkage, improve compression set slightly, and cause no loss in tensile strength or elongation.

Bonding—Silicone rubber can be bonded to most materials other than plastics and organic rubbers. Bonding techniques differ depending on whether the silicone rubber is cured or uncured. To bond uncured silicone rubber to metal, glass or ceramic (or to another uncured silicone rubber) the two materials (with clean surfaces) are placed in contact and molded together by means of the normal silicone curing schedule described previously. An improved bond can often be obtained by applying a silicone resin primer to the nonsilicone surface and allowing it to air-dry before bringing the two materials into contact. To bond cured silicone rubber to a solid nonsilicone material or to another cured silicone rubber, the two materials (with clean surfaces) are brought together under pressure with a 5-15 mil sheet of thoroughly-worked uncured silicone rubber between them. The sandwich is then subjected to the normal silicone curing cycle. A 5-10 mil layer of silicone rubber paste may be used instead of the uncured sheet, and improved adhesion may often be obtained by means of a silicone resin primer. This method is also suitable for joining two nonsilicone materials with a silicone rubber adhesive.

Silicone specialties

The bonding methods described above are not always feasible, and a variety of silicone adhesives have been developed. These adhesives can be brushed on to the surfaces to be joined and cured to provide good bond strengths. Some of them require a heat-and-pressure cure, but others, if allowed to air-dry before the parts are pressed together, will cure at room temperature under contact pressure. A recently developed adhesive, for example, develops good bond strength within 24 hr and maximum strength within 3-7 days. It has good heat stability and creep strength up to 212 F. It will bond silicone rubber to itself or to aluminum, magnesium, stainless steel, butyl synthetic rubber or saran rubber. Its bond with silicone extrusions is better than its bond with silicone moldings. Specifically, a peel strength of 15 lb per in. has been obtained between extruded silicone and aluminum, compared to a peel strength of 9 lb per in. between molded silicone and aluminum.

A pressure-sensitive silicone adhesive is also available for application to tape. Pressure-sensitive silicone adhesive tape is expected to be useful as electrical insulation.

No article on silicones would be complete without some reference to the most widely known silicone of them all—bouncing putty. That strange material became an interesting novelty because of its ability to deform as a plastic material in response to slow, mild pressure, to bounce as an elastomeric material when dropped, and to shatter as a brittle material when struck a hard blow. For some time it seemed there were no practical applications for the material, but in recent years a few have been discovered. Among the most important are cores for golf balls, leveling pads for furniture, and a clutch fluid.

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Firestone Tire and Rubber Co., Akron, Ohio
Midland Industrial Finishes Co., Waukegan, Ill.
Minnesota Rubber and Gasket Co., Minneapolis, Minn.
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DOW CORNING CORPORATION

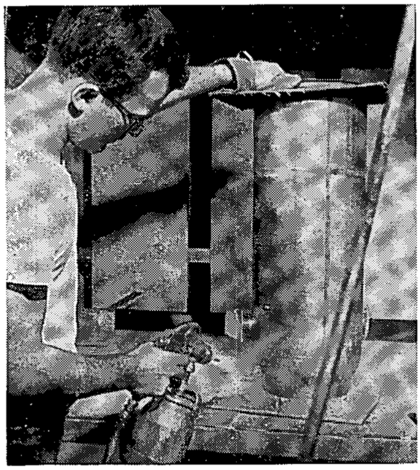
Silicone News

FOR DESIGN ENGINEERS No. 13

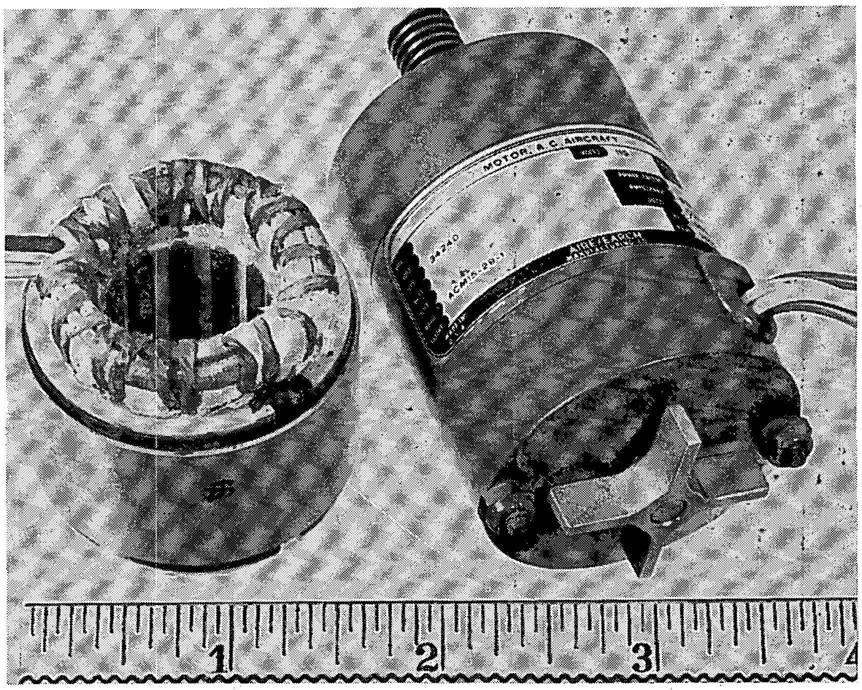
Silicone Aluminum Paint Protects Jet Engine Combustion Chambers

The materials used in many of the combustion chambers and burner supports manufactured for J-35 jet engines by Solar Aircraft of Des Moines, must remain unaffected by abnormally high temperatures. Aluminum clad steel solves the problem satisfactorily with exception of various fusion welds. These must be recoated with aluminum or a noncorrosive coating that will withstand up to 800 F.

Solar engineers have the answer to that problem, too. They simply spray or dip the welded part with two coats of Sicon, an aluminum paint formulated with Dow Corning silicone resins by Midland Industrial Finishes.



After a one hour bake at 400 F, the silicone based coating provides the required protection. According to Solar, this is one of the most satisfactory paints for use on jet engine parts. *No. 127*



SILICONE INSULATION ADDS LIFE, CUTS SIZE OF MINIATURE MOTOR IN B-52A BOMBER

PROBLEM:

Ambient temperatures range from —65 to 300 F.

Size and weight must be held to a minimum.

Maximum reliability is imperative.

To meet those requirements, design a miniature a-c motor for continuous duty in the oil temperature controller for the Boeing B-52A Stratofortress.

SOLUTION:

Design engineers with the AiResearch Manufacturing Division of The Garret Corporation found the best solution to that problem in electrical insulating materials and high temperature paints made with Dow Corning silicones. Dow Corning 33 Grease solved the bearing problem.

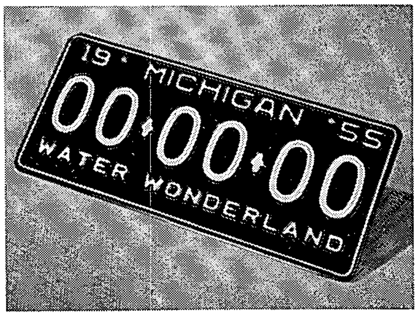
A silicone bonded asbestos-glass laminate, made by the Irvington Varnish and Insulator Company is used for slot and phase insulation. Dow Corning Sylkyd enameled magnet wire, manufactured by Hi-Temp Wires, Inc. is used in the windings. Silicone-glass laminate is used for end laminations and slot wedges. End connections are tied with Silastic-impregnated glass cord.

Silastic-impregnated Turbo 117 glass sleeving, made by William Brand and Company, is used to insulate the connections because of its flexibility and outstanding resistance to fraying.

(Cont. pg. 2)

SILICONES IMPROVE LICENSE PLATE APPEARANCE AND SERVICE LIFE

Next time you see one of the 4,000,000 vehicles bearing the white on green 1955 Michigan license plate, note the smoothness and gloss of the green background. That's because the paint, supplied by the Saginaw Paint Company of Saginaw, Michigan, was formulated with Dow Corning 200 Fluid. Addition of less than 1% of the silicone fluid helped reduce sags and wrinkles during dipping and increased color retention and resistance to weathering and snow removal chemicals. *No. 128*



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MORE

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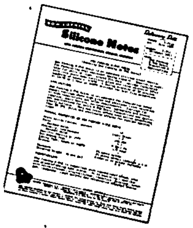
Silicone News

DOW CORNING PUBLICATIONS ON NEW DEVELOPMENTS AND TECHNICAL DATA . . .



New 1955 Reference Guide to Dow Corning silicone products gives in 8 pages a brief but comprehensive summary of the properties and applications for the silicone products that are most widely used. Products are indexed by type of application. With increasing effort devoted to product improvement and cost reduction, such a reference guide to this remarkably stable group of engineering materials becomes increasingly important to design, production and maintenance engineers. *No. 132*

◆

Silicone Foaming Powders produce heat-stable, nonflammable, easily machined, low density foam structures for electrical and thermal insulation. Supplied ready to use, they can be foamed in place and often cured in service. Recently published data sheet gives applications, properties and foaming characteristics. *No. 133*

◆

Dow Corning R-4010 Resin is a silicone water repellent coating that markedly improves wet insulation resistance of Class A or Class B electrical equipment. Easily applied by dipping, spraying or brushing, it air dries tack-free in 20 to 30 minutes and cures within 24 hours. *No. 134*

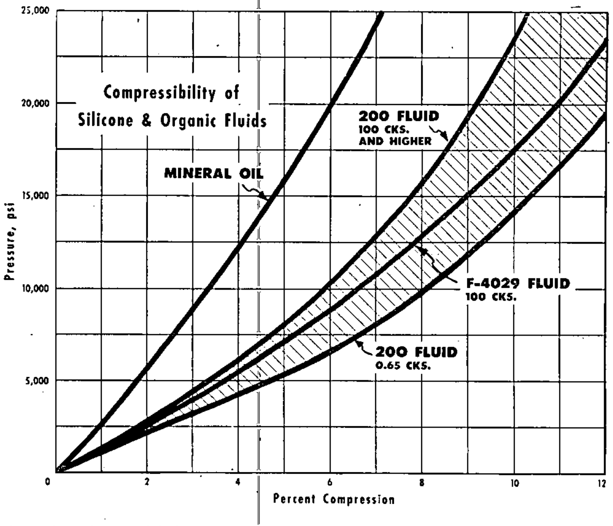
◆

"New Developments in Silicones" is a 16 page progress report which appeared in a recent issue of MACHINE DESIGN. A complete review of the silicone products most useful to designers, the article provides data and illustrates applications for silicone foams, protective coatings, rigid laminates, dielectrics, lubricants, rubber and adhesives. Reprints available. *No. 135*

◆

Dow Corning 36 Emulsion is a completely new silicone mold lubricant. Much more stable than any comparable silicone emulsion, it gives molded parts a superior surface finish. Its stability is attributable to an average particle size of less than 0.5 microns. At concentrations in the range of 1 part emulsion to 100-200 parts water, Dow Corning 36 Emulsion gives clean, easy release of rubber or plastic moldings and cast metal parts. *No. 136*

DESIGNERS USE SILICONE FLUIDS FOR MORE EFFICIENT SPRINGING



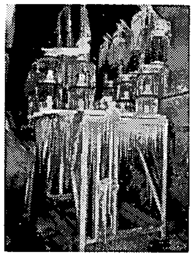
Dow Corning silicone fluids have always been noted for their thermal stability and their remarkably flat viscosity-temperature slopes. They have, therefore, been widely used as damping media in such devices as dashpots, overload relays and torsional vibration dampers for crankshafts.

More recently, designers have found that certain silicone fluids, Dow Corning F-4029 and some Dow Corning 200 Fluids, also have high compressibility. Using these fluids, engineers have produced liquid springs and shock absorbers with the same capacity as much larger and heavier metal coil springs. Testing indicates these highly compact liquid springs retain a high order of efficiency even under constant recycling at milli-second intervals.

As shown in the graph, both Dow Corning F-4029 and the Dow Corning 200 Fluids are more compresible than the mineral oil commonly used in liquid springs. At 20,000 psi, F-4029 has a compressibility of 10.8% which is mid-way between that of Dow Corning 200 Fluids of the same and of lower viscosity grades. While it lacks the compressibility of the lower viscosity 200 Fluids, Dow Corning F-4029 is less volatile and has a lower viscosity-temperature coefficient. *No. 130*

Westinghouse Seals New Switches With Silastic for Sub-zero Service

Sealed, top and bottom, with Silastic gaskets, the new Westinghouse gas-filled, load interrupter switches remain operable at temperatures as low as —65 F. Organic rubber seals were originally tried, but sub-zero weather caused the seals to harden and shrink, allowing the sulfur hexafluoride gas to escape.



On testing, Westinghouse engineers found that Silastic gaskets easily passed all pressure, vacuum, and temperature requirements, and were not affected by the gas. The Silastic gaskets provide such a tight seal that Westinghouse expects the units to hold gas pressures of 30 psi indefinitely without recharging. *No. 131*

MINIATURE MOTORS *(Continued)*

The stator is impregnated with Dow Corning 997 silicone varnish and baked at 400 F. The stator bore is painted with Sicon black silicone enamel, manufactured by Midland Industrial Finishes.

The ball bearings are lubricated with Dow Corning 33 silicone grease to give long service at temperatures ranging from —65 to 300 F. *No. 129*

Dow Corning Corporation, Dept. 7002, Midland, Michigan
Please send me: 127 128 129 130 131
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