Stabilization of Silicone Lubricating Fluids above 200° C. by Iron, Copper, Cerium, and Other Metal Compounds

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IN LUBRICANT applications of silicone liquids the upper temperature limit of usefulness is frequently set by the tendency to form rubbery gels. This not only deprives the bearing of the essential liquid phase, but hampers relubrication. Some means of delaying or preventing gelation is urgently required to extend the usefulness of these remarkable liquids in the 200° to 300° C. range. A laboratory survey (*2*) of conventional oxidation inhibitors and of several classes of materials not usually classed as inhibitors showed that aromatic amines, phenothiazines, and organic selenides prolonged the life of silicone oils two to five times, and some finely dispersed solids and metallo-organic compounds showed unexpected stabilizing effects, one of which led to development of a new-type inhibitor of spectacular effectiveness—the subject of the present report.

The survey included disalicylalethylenediamine (DSED) and disalicylalpropylenediamine (DSPD), supplied as metal deactivators, with particular reference to copper, and stated by the manufacturer not to be antioxidants. Nevertheless, when tested with a lightly phenylated silicone, they equaled or excelled the better conventional antioxidants such as phenyl-1-naphthylamine. Volatilization rates were lowered and the time to gelation was extended to eight times that of the control. The most unusual properties of these inhibitors, however, became apparent only when they were tested in the presence of extensive surfaces of common metals. The presence of cold rolled steel increased the life of the inhibited fluid by about 50% and copper by over 100% (to approximately 30 times the life of the uninhibited control). Brass showed no effect, and aluminum decreased the effect of the inhibitor.

Both iron and copper showed signs of chemical reaction with the metal deactivator to give dispersible compounds, so portions of the DSPD were allowed to react with copper oxide and with oil-soluble copper soaps. When these reaction products were tested as inhibitors, an optimum Cu^{++}-DSPD ratio increased the life of a lightly phenylated silicone fluid at 250° C. (482° F.) from 150 to 1800 hours. Specialized inhibiting procedures are essential, if the maximum stabilizing effect is to be realized. The somewhat erratic results obtained with different lots of DSPD and DSED before deliberate introduction of metal ions were shown by spectrographic analyses to result from variable traces of iron introduced during preparation of the compounds. Purified materials were less effective inhibitors.

Several metals commonly known to be redox catalysts in organic systems gave no better results than iron or copper in the presence of DSPD. Iron, cobalt, nickel, and copper compounds have been patented as stabilizers for silicone fluids (*3*). A survey of the behavior of the new-type iron and copper inhibitors under a wide range of conditions revealed one serious problem. While the inhibited silicones showed excellent stability in the presence of excess oxygen and adequate ventilation, in oxygen-deficient closed systems the cupric ion was reduced to Cu_2O or to metallic copper which separated as a solid phase. The ferric ion was partly reduced to the ferrous state, and formed a dense black suspension. A reconsideration of the redox chemicals available led to a test of cerium ions. The cerium complexes not only eliminated separation of the inhibitor under oxygen-deficient conditions, but were an order of magnitude more effective than even the copper complexes, so further investigation was centered on the preparation and properties of the cerium-inhibited silicones. The processes involved in metal compound stabilization of silicones differ in important aspects from those of conventional oxidation inhibitors. The chemistry of this novel inhibitory process is now under study and will be reported separately.

MATERIALS

The silicone liquids studied include most of the chemical types of interest for high-temperature lubrication (Table I). A major part of the work was done with products of a single manufacturer. When similar products of two or more manufacturers are discussed under comparable conditions, nonidentifying code designations are employed. Because of its excellent low-temperature properties, much of the investigation has dealt with a slightly phenylated 50-cs. oil. A DC 510-50-cs. silicone was also stripped on a Consolidated Electrodynamics Corp. Type CMS-14 centrifugal still to secure a less volatile fraction of silicone. Figures 1 to 10 are based on experiments with DC 510-50-cs. silicone. Some physical properties of the still fractions are given in Table II.

TEST PROCEDURES

Materials Used	Source
Disalicylalethylenediamine (DSED)	Rubber Chemicals Section, Du Pont Co.
Disalicylalpropylenediamine (DSPD)	
Disalicylal-*o*-phenylenediamine	
Acetylaminophenol	
Disalicylalbenzidine	Naval Research Laboratory
N,N'-Dibenzylidine-ethylenediamine	
N,N'-Dicinnamylidene-ethylenediamine	
2-(1-Hydroxybenzyl)benzamidazole	
p-Aminophenol	Tennessee Eastman
$CeCl_3 \cdot 7H_2O$	G. Frederick Smith Chemical Co. reagent grade
$Ce(SO_4)_2$, purified (anhydrous)	Fisher Scientific Co.
Lanthanum chloride (99.99%)	Lindsay Chemical Co., West Chicago, Ill.
Praseodymium chloride (99.0%)	
Ytterbium chloride (99.0%)	
Europium chloride (98.99%)	

Petri Dish Test. The silicone fluid (50 grams) was exposed in a Petri dish in a convection oven at 250° or 300° C. The dishes were 9 cm. in diameter, of molded borosilicate glass, and had approximately plane parallel bottoms. Oven temperature was maintained within ±1° C. with a recording controller, and the test samples were placed symmetrically on a half-inch-thick aluminum plate to assure temperature equivalence. To ensure reproducible results, this plate was manually rotated at regular intervals to expose each sample in turn to conditions at a given point in the oven.

Table I. Silicone Fluids Studied

Type	Designation	Degree of Phenylation	Nominal Vis. at 25° C., Cs.
Methyl silicone	A-50	None	50
	B-100	None	100
	C-100	None	100
	D-70	None	70
Methyl phenyl silicone	DC 510-50	Light	50
	DC 510-100	Light	100
	DC 510-500	Light	500
	E-100	Light	100
	DC 550	Moderate	100
	DC 710	High	500
Chlorine-modified methyl phenyl silicone	F-70	Light	70
	G-60	Light	60

Table II. Physical Properties of DC 510-50 Silicone after Stripping in Centrifugal Still

Fraction	Rotor Temp., ° C.	% Yield	n^{20}	Vis. 100° F., Cs.
0	Initial silicone	...	1.4248	39.22
1	100	0.1	1.4230	10.08
2	110	0.5	1.4223	8.19
3	125	2.2	1.4214	9.58
4	140	4.9	1.4224	10.81
5	150	3.6	1.4232	12.25
6	163	5.4	1.4225	14.22
7	175	11.4	1.4247	17.40
8	190-200	5.0	1.4250	20.94
9	Stripped residue	66.9	1.4257	58.94

Changes in the silicone liquid were followed by determining the volatilization loss at suitable intervals, and by successive measurements of viscosity at 25° C. (2). In most cases the time elapsed before gelation of the liquid was also recorded. The transition from a viscous liquid to an elastic nonflowing gel was relatively sharp. For a liquid life of 100 hours or less the transition time did not exceed an hour. For more stable liquids an unambiguous change occurred in less than 5% of the total time to gelation. A control sample of uninhibited liquid was exposed with every group of test samples.

This test provides ready access of oxygen and continuous removal of volatile products by convective action and oven ventilation. The surface-volume ratio is significant. Tests conducted in dishes of smaller diameter gave comparable results, if the depth of liquid was the same as in the standard procedure. The effect of surface-volume ratio on silicone life with simple convective ventilation is shown in Figure 1.

Thin Film Test. The test was devised to permit more rapid estimates of silicone stability than the previous test and study of smaller samples. In this test 0.15 gram of the liquid was spread over the bottom of a 5- or 6-cm. Petri dish and exposed in a convection oven as for the standard Petri dish test. Volatilization loss was followed by periodic weighing, and the elapsed time to gelation was recorded. Only qualitative observations of the changes in viscosity were possible.

The thin film test emphasizes availability of oxygen and rapidity of removal of volatilized products more than the Petri dish test. At 300° C. the life of an uninhibited 510-50 liquid in the thin film test is 2 hours, instead of the 19 hours in the Petri dish test.

Aeration Test. Fifteen grams of silicone was placed in a 1.6 x 46 cm. borosilicate glass tube, the lower 17 cm. of which was inserted in an electrically heated aluminum block. The surface of the liquid was 1 or 2 cm. below the surface of the block at the test temperature. Clean dry air was bubbled through the liquid at the rate of 50 cc. per minute. The geometry and flow rate are similar to those in the test for the corrosiveness and oxidation stability of light oils (*4*), but the water-cooled condenser and metal strips were omitted. Under the conditions of the experiment, the presence or absence of a water-cooled condeners had little effect on test life.

Ventilation and Stagnation Tests. The ventilation test was a modification of the aeration test, in which the space above the liquid was purged by 50 cc. of air per minute, introduced just above the liquid surface. In the stagnation test the air stream was omitted, but the tube was left open to the air at the top; the fog of silicone volatilization products remained mostly in the tube and gradually collected on the walls by diffusion. The deposited liquids drained back into the test sample.

EXPERIMENTAL RESULTS AND DISCUSSION

Inhibition Procedure. The procedure for securing the maximum inhibiting effect with metal compounds is a complex one developed by trial and error.

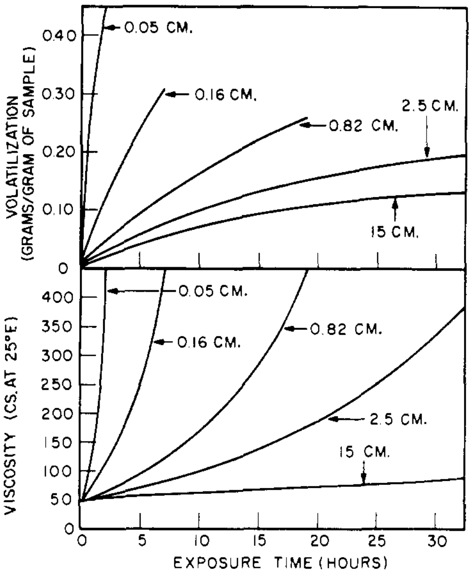

Figure 1. Deterioration of silicone at 300° C. as a function of sample depth

No inhibitor

The metal ion (usually as an oil-soluble soap) is combined with DSPD in a hydrocarbon solvent to form a soluble chelate. Chelate formation occurs readily in toluene or xylene at the boiling point of the solvent.

The silicone is added to the solution of chelate and the mixture is heated in a well-ventilated oven while bubbling with air to remove the hydrocarbon solvent. This leaves the metal chelate as a dark opaque suspension in the silicone, nearly nonsettling and nonfilterable.

This suspension is heated at 285° C. while a vigorous stream of air is passed through it. The system first becomes almost black, then slowly clears to light yellow, green, or orange, according to the metal ion present. Properly inhibited systems are slightly turbid. Only a minor amount of insoluble material remains in the bottom of the vessel. During this heating and aerating stage, which may require from 12 to 72 hours to yield a clear preparation, a substantial fraction of the silicone is lost by volatilization. This may reach 35% for a DC 510-50 oil as received. It will be less (5 to 15% loss) for a silicone liquid stripped in a molecular still or one of higher molecular weight such as silicone DC 510-100. The silicone liquid also increases in viscosity during inhibition treatment. Volatilization and viscosity changes are shown as a function of time in Figure 2. Marked stabilization occurs from the very beginning of the treatment. This is made particularly evident by the fact

Table III. Effect of Initial Form of Combination of Metal Ion on Inhibitory Behavior of Copper, Iron, Cerium, and Chromium

(Petri dish tests at 300° C. DC 510-50 silicone)

Additive	Additive, %		Hours to Gel.	Vol. Loss, %	Improvement Factor (Gel.)
	Metal cmpd.	DSPD			
Control	None	None	19	26	. . .
		Copper Compounds			
DSPD alone	. . .	1.0	196	38	10
	. . .	3.0	261	48	14
+ Cu metal	. . .	3.0	595	65	31
+ oxidized copper	. . .	1.0	420	44	22
+ Cu (DNNS)	0.2	1.8	362	41	19
+ Cu oleyl salicylate	0.5	2.5	1794	53	94
+ Cu DSPD	0.3	2.7	2380	63	125
+Cu toluate	0.2	1.8	1008	74	53
Cupric oleate	1.0	. . .	357	52	19
Copper DSPD	3.0	. . .	67	30	4
		Iron Compounds			
DSPD + soft steel metal	. . .	3.0	144	44	8
+ hard steel metal	. . .	3.0	310	55	16
+ rusted steel	. . .	1.0	330	42	17
Ferric valerate	1.0	. . .	336	42	17
	3.0	. . .	712	48	37
Ferric caproate	1.0	. . .	1560	67	82
Ferric 2-ethyl hexanoate	1.0	. . .	1640	73	86
Dimethyl ferrocene	3.0	. . .	65	37	3
+ DSPD	0.2	0.8	120	50	6
Ferric valerate + DSPD	0.5	1.0	1680	76	88
		Cerium Compounds			
Cerous toluate alone	1.0	. . .	48	28	2
DSPD					
+ cerous toluate	0.1	0.9	>2160[a]	(81)	(>114)
+ cerous toluate	0.2	0.8	>1440[a]	(37)	(>76)
+ceric toluate (basic)	0.2	0.8	>1440[a]	(41)	(>76)
+ cerous DNNS	0.1	0.9	>1560[a]	(73)	(>82)
Cerous DNNS, alone	1.0	. . .	144	34	8
DSPD + chromium toluate	0.2	0.8	408	53	21

[a] Measurement originally made to clarify a question resolved when test reached life shown. Because of extremely long time required for ultimate failure of more stable oils, test discontinued to make way for another experiment.

that the viscosity of the inhibited liquid increases by only 3 cs. during the time required for the untreated or control liquid to gel. This repression of the cross-linking reactions responsible for viscosity increase and gelation also characterizes the inhibited fluids during later high-temperature exposure. Thus, in the thin film test as much as 95% of the liquid may be volatilized during a 1000-hour exposure at 300° C., but the residue will still be liquid.

Factors Influencing Choice of Process Solvent. The organic liquid in which the chelate is formed should be a good solvent. Toluene and xylene were satisfactory, but oxygen-containing liquids such as 2-propanol, methanol, or acetone prevented inhibition and led to premature gelation of the silicone oil during heat treatment. Hence properties other than solvent power are important for the carrier liquid.

Metal Carrier. Although combination of the metal ion with DSPD or a closely analogous compound such as DSED or disalicylal-*o*-phenylenediamine gave the best inhibiting action, processes in which the metal was brought into solution in association with other organic structures led to significant but less striking stabilization. Table III lists copper, iron, and cerium compounds used with varying success. In the case of fatty acid salts, a large part of the metal separated as an insoluble precipitate early in the heat treatment. The dinonylnaphthalene sulfonates required an excessive period of heating at 285° C. to clarify the liquid, and the stable life of the resulting oil was only 10% of that produced with the same metal ion and DSPD.

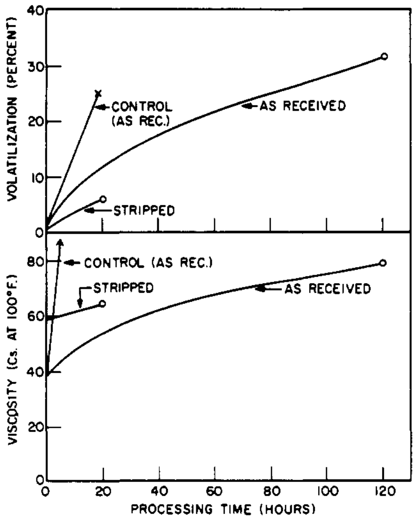

Figure 2. Processing of silicone as received and after stripping in molecular still 285° C.

Inhibitor, 0.2% cerium toluate + 0.8% DSPD
X. Gelation at time shown
o. Completion of inhibition process to give clear liquid at time shown
Controls contained no cerium or DSPD but processed same otherwise

Other compounds with structural resemblances to DSPD and DSED were also examined. Inhibition varied from moderate to negligible for the following compounds (listed in order of decreasing effectiveness).

Disalicylal-*o*-phenylenediamine
Disalicylalbenzidine
N-Salicylidenebutylamine
N,N'-Dibenzylidine-ethylenediamine
N,N'-Dicinnamylidene-ethylenediamine
Acetylaminophenol
p-Aminophenol
2-(1-Hydroxybenzyl)benzamidazole

Oxygen Supply. Aeration of the reaction mixture during heating is important because oxygen is essential to inhibition. If the liquid is stirred with an equivalent current of nitrogen, the initial black color does not clear up; the silicone volatilizes rapidly and leaves a highly viscous residue. Aeration with oxygen-enriched air (50% O_2) produces a clean, fully inhibited liquid in about half the normal time. The air stream has another important function; it carries away the volatile products formed during inhibition, together with small amounts of volatiles originally present. Any arrangement which condenses these products and returns them to the oil under treatment prevents inhibition and leads to premature gelation of the silicone. When the oil to be inhibited is contained in a half-filled Erlenmeyer flask, the minimum air flow rate for good inhibition is 100 cc. per minute per 100 ml. of silicone present. More rapid flow rates moderately shorten the time required for clearing the oil.

Optimum Temperature for Inhibition. The optimum temperature for inhibition was about 285° C. At lower temperatures the clearing reaction became tediously slow. Above 300° C. thermal decomposition leads to rapid oxidation and gelation of the silicone in spite of the inhibitor components present. The 285° C. temperature provides leeway for accidental fluctuations in heating control and possible hot spots in the processing equipment. Better results were obtained with a rapid initial heating of the liquid to treatment temperature, than when the reaction mixture was placed in an oven already at 285° C.

Effect of Initial Concentrations of Inhibiting Agents. Regardless of the quantities of metal salts used in processing, the amount that can be incorporated into the silicone fluid depends upon the type of silicone being inhibited. The quantity of metal ion dispersed varied from about 0.02% in the all-methyl silicone to about 0.2% for the highly phenylated fluids.

In processing a silicone fluid a ratio of 1 mole of cerium to about 18 moles of DSPD gives excellent preparations. Initial concentrations of 0.1 and 0.2 gram of cerous toluate and 0.9 to 1.8 grams of DSPD per 100 grams of silicone fluid are satisfactory. The higher concentrations require longer processing.

Effect of Volatile Content. In the case of the lightly phenylated DC 510 silicones the time required for inhibition (time to clearing) was greater when the proportion of volatiles present was larger. The residue from stripping about 30% of volatiles from the DC 510-50 liquid in a molecular still could be inhibited in a much shorter time than the original oil as received. The DC 510-100 liquid, which as received contained a smaller proportion of volatiles, was also more quickly cleared. Quantitative effects are reported in Table IV.

General Characteristics of Metal-Inhibited DC 510-50 Silicone. The cerium-processed silicones are orange to straw-colored liquids which show a characteristic haze or turbidity. Filtration through low-adsorbency filters with openings of 5 microns or larger has a negligible effect on stability; filtration through a 1-micron filter reduces the stability appreciably, but the filtered material still has a life 50 to 100 times that of the control. At least a part of the inhibiting substance is evidently a submicronic colloid.

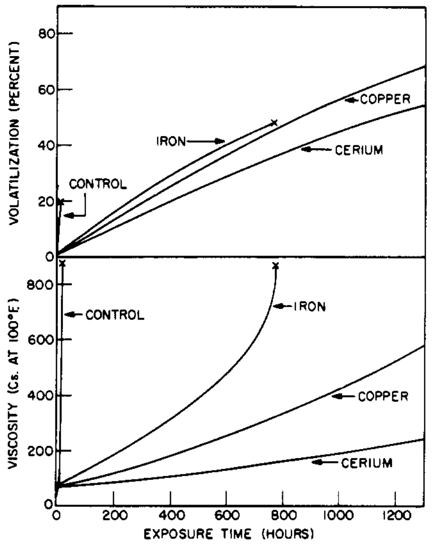

Figure 3. Inhibition by metal toluates in silicone

Aeration test at 300° C. 0.2% metal toluate + 0.8% DSPD
X. Gelation at time shown

Table IV. Relation between Volatiles Lost and Time Required to Process Fluid

(100-gram samples)

DC 510-50	Treatment Time, Hours	Vol. Loss during Treatment, %
As received	72	31
NB 100	48	21
Stripped	24	6

The inhibited liquids have viscosities from one and one half to twice that of the starting material. On exposure to oxidizing and volatilizing conditions at 300°, further evaporation or increase in viscosity occurs at very low rates as compared to the untreated silicone. Figure 3 graphically compares the viscosity increase and volatiles loss of the control with those of the liquid inhibited with iron, copper, and cerium compounds.

Figure 4 shows the behavior of the same systems under less vigorous oxidizing and volatilizing conditions. Here the superiority of the cerium treatment over the iron or copper inhibitors is even more pronounced. Iron and copper also exchange relative positions.

The improvement factor for the inhibited silicone varied with the nature of the test applied and with performance criterion chosen. Using the thin-film time to gelation, optimum cerium inhibition will give at least 500 times the liquid life shown by the control. Viscosity increase during the first 1000 hours of the aeration test (Figure 3) proceeds at one sixtieth the rate at which the control makes the same increase.

In the same test the initial evaporation rate of the cerium-inhibited compound is one twentieth that of the control. Comparisons based on initial rates are less impressive than comparisons of time to gelation because, after a short life, the uninhibited silicone shows a runaway viscosity increase that terminates in gelation. On the other hand, the cerium-inhibited liquids volatilize and thicken very gradually, showing no break point or runaway behavior.

Relative Stabilization Produced by Different Metals. In view of the pronounced stabilizing effects of iron, copper, and cerium, compounds of a wide selection of metals were tested for possible inhibitory effects in the presence of DSPD (Tables III and VI through XI). Significant effects were found for chromium and some rare earth compounds. Comparable thin film tests of copper, iron, and cerium as inhibitors are presented in Figure 5. Iron, copper, and cerium compounds are outstanding; praseodymium and europium compounds are slightly less so. Chromium, lanthanum, and ytterbium gave only slightly greater silicone life than DSPD alone. Compounds of the following metals gave negligible improvements in silicone stability or accelerated deterioration (in order of decreasing effectiveness): tin, barium, nickel, cobalt, vanadium, titanium, zinc, manganese, aluminum, and lead.

The oil-soluble aluminum compounds were notable because they caused gelation of the silicone liquid during the first 22 hours of inhibition. The volatilization loss at this time was 86%, compared with about 25% for the uninhibited control during 19 hours at 300° C. Lead and manganese ions also caused premature gelation and excessive volatilization. Barium ion did not accelerate volatilization but it completely cancelled the protective action of the DSPD, so that the liquid gelled after 22 hours.

When the corresponding free metals were heated with DSPD and silicone, similar but less pronounced deleterious effects were noted. In the absence of free DSPD—e.g., in

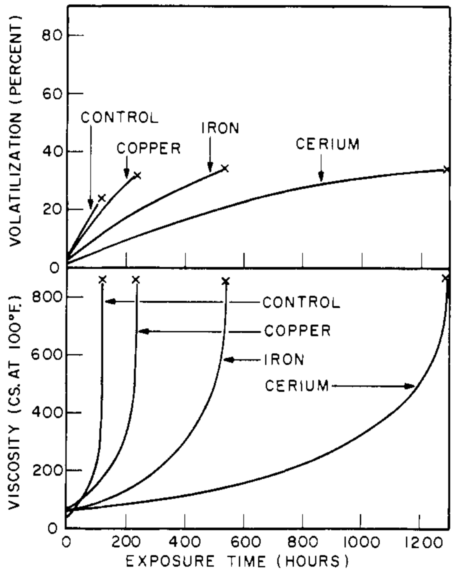

Figure 4. Inhibition by metal toluates in silicone

Ventilation test at 300° C.
0.2% metal toluate + 0.8% DSPD
X. Gelation at time shown

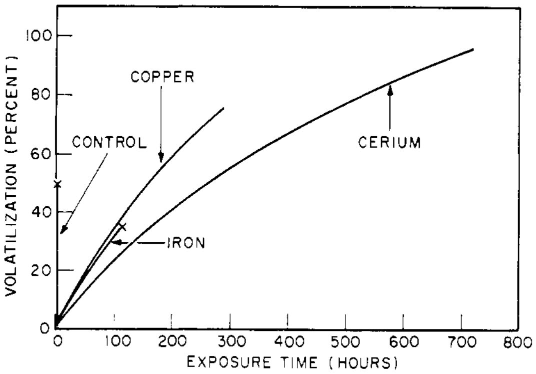

Figure 5. Inhibition by metal toluates in silicone

Thin film test at 300° C.
0.2% metal toluate + 0.8% DSPD
X. Gelation at time shown

Table V. Inhibitory Behavior of Metal Ions in Silicone Fluids

(Petri dish test at 300° C.)

Silicone Fluid	Additive	Additive, % Metal compd.	DSPD	Hours to Gel.	Vol. Loss, %	Improvement Factor (Gel.)
Methyl A 50	Control	None	None	13	19	. . .
	Copper toluate + DSPD	0.1	0.9	360	47	28
	Ferrous + DSPD	0.1	0.9	264	41	20
	Cerous + DSPD	0.1	0.9	> 720[a]	(32)	(> 55)
Methyl phenyl DC 510	Control	None	None	19	26	. . .
	Copper toluate + DSPD	0.1	0.9	1008	74	53
	Ferrous + DSPD	0.1	0.9	1344	77	71
	Cerous + DSPD	0.1	0.9	> 2160[a]	(53)	(> 113)
DC 550	Control	None	None	70	41	. . .
	Copper toluate + DSPD	0.1	0.9	552	53	8
	Ferrous + DSPD	0.9	0.9	432	51	6
	Cerous + DSPD	0.1	0.9	> 768[a]	(47)	(> 11)
DC 710	Control	None	None	183	53	. . .
	Copper toluate + DSPD	0.1	0.9	432	56	2
	Ferrous + DSPD	0.1	0.9	360	47	2
	Cerous + DSPD	0.1	0.9	720	61	4
Chlorine-modified methyl phenyl, F-70	Control	None	None	16	24	. . .
	Copper toluate + DSPD	0.1	0.9	264	51	16
	Ferrous + DSPD	0.1	0.9	216	47	13
	Cerous + DSPD	0.1	0.9	360	56	22
G-60	Control	None	None	16	17	. . .
	Copper toluate + DSPD	0.1	0.9	192	29	12
	Ferrous + DSPD	0.1	0.9	168	27	10
	Cerous + DSPD	0.1	0.9	216	31	13

[a] Test not continued to gelation; see [a], Table III.

Table VI. Effect of Oxygen Supply on Stability of Metal-Inhibited DC Silicone at 250° C.

(Standard inhibition procedure at 250° C. prior to testing)

	Additive, %		Aeration Test		Ventilation Test	
Additive	Metal cmpd.	DSPD	Hr. to gel.	% vol.	Hr. to gel.	% vol.
Control	None	None	130	30	576	18
Copper DSPD[a] + DSPD	0.5	1.0	>1320[b]	(56)	480	21
Copper toluate + DSPD	0.2	0.8	>1060[b]	(47)	384	15
Ferrous toluate + DSPD	0.2	0.8	>720[b]	(34)	912	18
Cerous toluate + DSPD	0.2	0.8	>1440[b]	(42)	>1440[b]	(17)
DSPD[c]	...	1.0	504	38	720	29
DSPD[c]	...	5.0	732	43	912	27

[a] Crystalline product of reaction of DSPD with excess cupric oxide.
[b] Test not continued to gelation; see [a], Table III.
[c] Not processed prior to testing.

Table VII. Relative Stabilizing Effect of Metal Ions on DC 510-50 Oil

(300° C. Standard inhibition procedure prior to testing)

	Additive, %		Aeration Test		Ventilation Test	
Additive	Metal cmpd.	DSPD	Hr. to gel.	% vol.	Hr. to gel.	% vol.
Control[a]	None	None	20	15	114	23
DSPD[a]		1.0	216	32	144	23
DSPD[a]		3.0	261	48	192	26
+ Cu DSPD	0.5	1.0	>1440[b]	(73)	216	22
+ Cu toluate	0.2	0.8	>1056[b]	(60)	240	30
+ oleyl salicylate	0.5	1.0	>1440[b]	(53)	240	30
+ ferrous toluate	0.2	0.8	768	47	528	34
+ferric 2-ethyl hexanoate	0.5	1.0	552	41	360	33
+ ferric valerate	0.5	1.0	408	35	192	29
+ cerous toluate	0.05	0.95	>980[b]	(47)	>600[b]	(28)
	0.1	0.9	>1780[b]	(67)	1288	35
	0.2	0.8	>1500[b]	(56)	>432[b]	(10)
	0.1	0.5	860	(43)	288	25
+ ceric toluate (basic)	0.05	0.95	>640[b]	(36)	216	23
	0.1	0.9	>1200[b]	(51)	>720[b]	(31)
	0.2	0.8	>1440[b]	(49)	>720[b]	(29)
+ praseodymium toluate	0.1	0.9	>408[b]	(39)	>336[b]	(21)
+ lanthanum toluate	0.1	0.9	480	41	168	23
+ ytterbium toluate	0.1	0.9	456	38	192	25
+ europium toluate	0.1	0.9	>336[b]	(37)	>336[b]	(23)
+ chromium toluate	0.2	0.8	240	37	120	23

[a] Not processed prior to testing.
[b] Test not continued to gelation; see [a], Table III.

Table VIII. Relative Stabilizing Effect of Metal Ions with DSPD as Carrier

[Silicone DC 510-50, lot JJ-124 (1958). Standard inhibiting process. Thin film test at 300° C.]

	Additive, %				
Additive	Metal cmpd.	DSPD	Hours to Gel.	Vol. Loss, %	Improvement Factor
Control	None	None	2	49	...
DSPD					
+ cupric toluate	0.2	0.8	>284[a]	(75)	(>140)
+ ferrous toluate	0.2	0.8	115	36	57
+ cerous toluate	0.2	0.8	>720	(96)	(>360)
	0.1	0.9	1032	97	516
	0.1	0.9	>288[a]	(67)	(>140)
+ ceric toluate (basic)	0.1	0.9	>384[a]	(83)	(>190)
+ praseodymium toluate	0.1	0.9	224	68	110
+ lanthanum toluate	0.1	0.9	24	67	12
+ europium toluate	0.1	0.9	236	71	120
+ ytterbium toluate	0.1	0.9	24	65	12
+ chromium toluate	0.1	0.9	120	43	60
+ tin toluate	0.1	0.9	24	63	12
+ barium toluate	0.1	0.9	24	57	12

[a] Test not continued to gelation; see [a], Table III.

the fully processed inhibited silicone—the free metals had negligible effects.

Response of Silicone Liquids to Inhibition by Cerous Toluate and DSPD. The susceptibilities to inhibition exhibited by five chemical different types of silicones liquids are shown in Table XI. (Because of the very short life of some of the control specimens in the thin film test, the improvement factors are subject to a larger uncertainty than in other tests and should be examined only for orders of magnitude.)

The slightly phenylated silicones such as DC 510-50, DC 510-100, and DC 510-500 and product E-100 show the longest test life after inhibition as well as the greatest improvement factor (300 to 500). The percentage improvements of the more highly phenylated liquids, such as the 550 and 710 types, were smaller although still noteworthy. Although originally more stable than the lightly phenylated material, their inhibited lives were shorter.

Table IX. Effect of Substrate on Thin Film Stability

[DC 510-50 silicone, as received. Lot JJ-124 (1958). Thin film test at 300° C.]

Substrate	SAE Classification	Hours to Gel.	Vol. Loss, %
Borosilicate glass	. . .	2	49
Soft steel	1020	10	36
Hard steel	52100	5	39
Copper	71	21	50
Aluminum	25	1	64

Table X. Effect of Percolation and Distillation on Stability

[DC 510-50 oil. Lot JJ-124 (1958). Thin film test at 300° C. Not inhibited]

Treatment	Hours to Gel.	% Loss
Oil as received	2	49
Percolated over alumina and silica gel	1	51
Residue, 1st mol. distillation	3	31
Residue, 2nd mol. distillation[a]	3	27
No. 7 fraction from mol. distillation (Table II)	0.5	71

[a] Residue from restripping portion of first distillation residue in smaller molecular still until yield of distillate became less than 0.05% per pass.

Some dimethyl silicones show spectacular improvement after inhibition, but their test lives, while now comparable with those of the more highly phenylated liquids, do not equal those obtained with the slightly phenylated type. Others, like C-100, gel during inhibition. Chlorophenyl silicones show negligible response or actually gel during inhibition. Dimethyl and chlorophenyl materials produced by different manufacturers have significant differences in response.

The differences reported for the various types may not be inherent properties of the major siloxane constituents of each, but may result from differences in the amount and nature of functional groups present in minor concentration. Such components can be expected to vary substantially from one product to another.

Effect of Ventilation and Oxygen Supply on Time to Gelation. Silicone liquids inhibited by the process reported are always unfavorably affected by the return of their volatilization products to the liquid under test, except when oxygen is completely excluded from the system. In the presence of oxygen, time to gelation is longest when the opportunity for volatilization and removal of deterioration products is greatest, as when the test liquid at 300° C. is swept by a stream of air or exposed with a high surface-volume ratio as in the Petri dish or thin film tests.

The equipment used in the aeration test permits wide variation of variables. Comparison between stabilities with vigorous sweeping of the liquid by passage of air bubbles and simple ventilation with an equal amount of air directed against the surface of the unstirred liquid is shown in Tables VI and VII. The untreated controls benefit from omission of bubbling contact and decrease in rate of oxygen availability, but all inhibited samples have longer life before gelation when the air is swept through the liquid continuously, in spite of the more intensive oxygen exposure that must accompany this treatment. In the aeration and ventilation tests the rate of return of volatilization products collected on the upper walls of the test tube should have

Table XI. Relative Effectiveness of Cerium as a Stabilizer for Chemical Types of Silicone Oils

(Standard inhibiting process with DSPD. Thin film test at 300° C.)

Silicone Type	% Cerous Toluate	Hours to Gel.	Vol. Loss, %	Improvement Factor
A-50 dimethyl silicone	Control	1	60	. . .
	0.1	312	87	312
B-100 dimethyl silicone	Control	1	37	. . .
	0.1	240	52	240
D-70 dimethyl silicone	Control	1	43	. . .
	0.1	264	58	264
DC 510-50 phenyl methyl, low phenyl	Control	2	49	. . .
	0.1	1032	97	516
DC 510-100 phenyl methyl, low phenyl	Control	3	33	. . .
	0.1	1152	84	384
DC 510-500 phenyl methyl, low phenyl	Control	3	24	. . .
	0.1	1488	79	496
E-100 phenyl methyl, low phenyl	Control	5	27	. . .
	0.1	864	96	173
DC 550 phenyl methyl, moderate phenylation	Control	63	71	. . .
	0.1	504	66	8
DC 710 phenyl methyl, heavy phenylation	Control	91	71	. . .
	0.1	264	33	2.9
F-70 chlorophenyl silicone	Control	24	68	. . .
	0.1	18	22	0.75
G-60 chlorophenyl silicone	Control	4	33	. . .
	0.1	[a]		

[a] Gelled during inhibition.

been the same. The effect of the refluxed volatiles as a separate factor was demonstrated by the following procedure. Duplicate samples of inhibited DC 510 silicone were exposed without stirring or forced air supply, as in the stagnation test. One sample was contained in the standard test tube used in the stagnation test and one in a similar tube cut off so that the mouth was flush with the surface of the heated block, instead of projecting 29 cm. With the shortened tube the fine fog of silicone vaporization products was completely carried away by atmospheric convection. In the longer tube much of this fog and vapor collided with the walls of the tube and flowed back to the test liquid.

The results are shown in Figure 6. To allow comparison with uninhibited materials, samples of untreated residue from molecular distillation were also exposed in long and short tubes. This oil was chosen as a control because it has a volatile content comparable with that of the inhibited oil obtained by processing DC 510-50 silicone as received. The samples in the short tubes lost volatiles more rapidly, but the inhibited liquid gelled more quickly in the long tube than in the short.

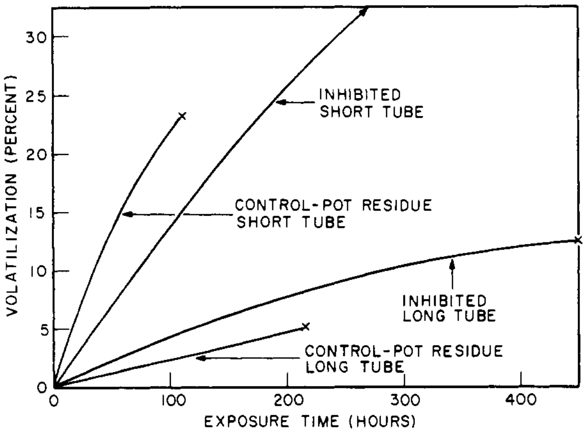

Figure 6. Deterioration of silicone fluid in short-form and tall-form test tubes at 300° C.

No aeration to either tube
0.1% cerous toluate + 0.9% DSPD
X. Gelation at time shown
↗ Jelled after 528 hours, with 52% volatile loss

Figure 7 and Table XII compare viscosity changes and volatilization losses in the aeration, ventilation, and stagnation tests. Volatilization loss is greatest in the aeration test and least in the stagnation test. Viscosity increases are in the reverse order, the change being least in the aeration test. Gelation takes place in the stagnation test, where the least amount of volatiles are removed, in just under 500 hours. In the ventilation test, where more volatiles are removed, gelation does not take place until just under 1300 hours, and in the aeration test, where removal of volatiles is excellent, no gelation takes place even in 1800 hours. In this time the viscosity has risen only to 300 cs.

Copper- and iron-inhibited preparations, heated to 300° C. in an oxygen-deficient environment or in a sealed tube, have the metal element present reduced to a lower valence or to the metallic state. This difficulty caused the search for other inhibiting metals that culminated in the development of the cerium treatment. Cerium-inhibited oils become less orange under reducing conditions at 300° C., but no precipitate settles out and the liquid regains its original color when oxygen is readmitted. Cerium has a marked advantage over iron or copper under such unfavorable conditions (Figure 8). Stability in reducing environments is an essential property of any oil additive intended for high temperature service because, at 300° or above, hydrocarbons or the hydrocarbon portion of siloxanes must be considered active reducing agents whenever access of atmospheric oxygen is prevented or seriously reduced.

In the case of the cerium-inhibited DC 510-50 silicone, the lack of an excess supply of oxygen was not harmful if decomposition products were swept away by an adequate supply of an inert gas such as nitrogen. Volatilization losses and viscosity increases were about half as large when commercial nitrogen was substituted for air in the aeration test. The behaviors with the two gases are compared in Figure 9. Commercial tank nitrogen usually carries less than 1.0 % of oxygen as an impurity—more than sufficient to produce the changes noted in the nitrogen-treated samples. It was exceedingly difficult to reduce the oxygen content of nitro-

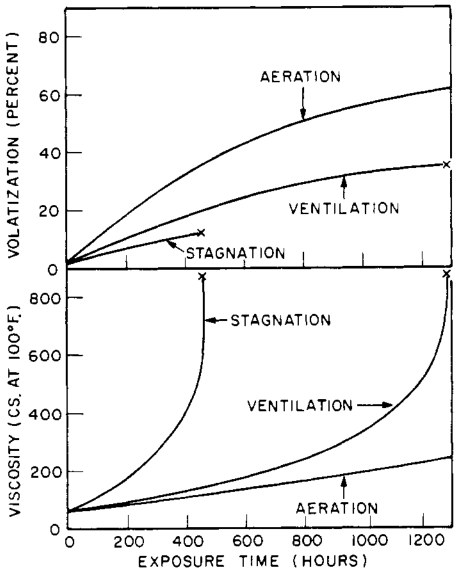

Figure 7. Aeration, ventilation, and stagnation tests at 300° C.

0.1% cerous toluate + 0.9% DSPD
X. Gelation at time shown

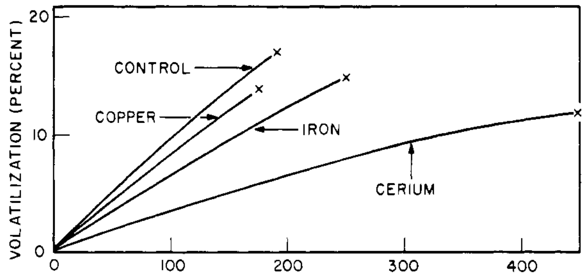

Figure 8. Inhibition by metal toluates in silicone in stagnation test at 300° C.

0.2% metal toluate + 0.8% DSPD
X. Gelation at time shown

Table XII. Viscosity Changes and Volatilization Losses

(Inhibited DC 510-50. 0.1% cerous toluate + 0.9% DSPD)

Exposure Time, Hours at 300° C.	Aeration Test		Ventilation Test		Stagnation Test	
	Vol. loss, %	Visc., cs. at 100° F.	Vol. loss, %	Visc., cs. at 100° F.	Vol. loss, %	Visc., cs. at 100° F.
Initial	...	64	...	64	...	64
100	10.0	80	5.0	85	4.0	123
400	31.5	110	17.0	135	11.0	400
500	37.5	125	20.5	155	Gel	Gel
800	50.5	160	28.0	245		
1200	60.0	225	34.5	515		
1300	61.5	240	Gel	Gel		
1800	67.0	300				

gen to a level where the large volume of gas passed through the sample did not cause small but significant increases in viscosity.

The cerium-inhibited silicones tolerate heating at 300° C. in an oxygen-free sealed container, either in vacuo or under nitrogen, with only a minor decrease in viscosity and without change in color or turbidity. This is analogous to the behavior of uninhibited silicones under similar treatment (*1, 5*) but in contrast to that of copper- or iron-inhibited silicones.

Effect of Temperature on Stability. The stability of a cerium-inhibited 510-50 silicone was examined from 300° to 371° C. (575° to 700° F.), the range in which pyrolysis has been reported to become an important mechanism of silicone degradation (*5*). Figure 10 shows that between 330° and 343° C. there is a sharp decrease in stability as measured by gelation time. Although cerium treatment improves stability throughout the whole range, the gains are much smaller at 343° C. (650° F.) and above. These data extend the generalization that gains from cerium inhibition are greatest in the aeration test where oxidation conditions are most severe, and substantially less for the stagnation test, in which the oxygen supply is limited. None of the treatments produce a detectable shift of the thermal decomposition threshold to higher or lower temperatures.

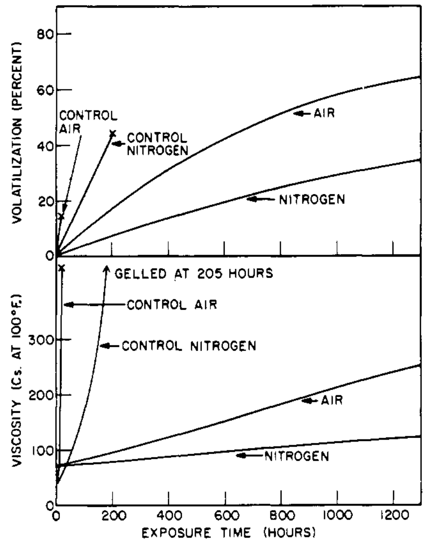

Figure 9. Effect of oxygen concentration in aeration test at 300° C.

0.1% cerous toluate + 0.9% DSPD

X. Gelation at time shown

Practical Significance. The improvements in silicone stability reported raise the temperature limit for prolonged use under oxidizing conditions from 200° or 250° to 300° C. The greatest improvements and the longest useful lives are obtained with lightly phenylated silicones having attractive low temperature viscosities and viscosity-temperature coefficients. Previously it was necessary to turn to moderately or highly phenylated oils, which were not useful at −65° F. and had much less desirable viscosity-temperature characteristics. These stabilized silicone oils may give the maximum gains in adequately ventilated applications. They should be especially valuable in situations involving severe oxidative exposure in bulk or in thin films. They will offer the least advantage in oxidative exposures involving collection and return of a major part of the volatiles evolved to the working liquid. However, the cerium-inhibited liquids should show 10-fold or better improvement even under unfavorable conditions.

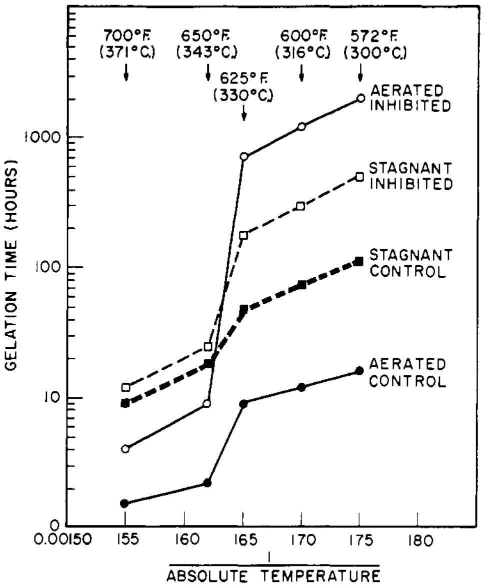

Figure 10. Stability of silicone as a function of temperature

0.1% cerous toluate + 0.9% DSPD

Careful functional and field testing will be required to identify suitable specific applications, but their general properties suggest consideration as jet engine lubricants, high-temperature hydraulic fluids, and heat transfer liquids. The lubricities of these stabilized silicone oils are essentially those of the starting silicones from which they were prepared. Improvements in stability have not been comparable for the halogen-containing silicones of better lubricity.

It has not yet been possible to formulate a high-temperature grease from the metal-inhibited oils which shows appreciably better high-temperature performance than a grease formulated from the original oil using a conventional antioxidant such as phenyl-1-naphthylamine. The inhibiting component is in all cases deactivated or adsorbed by the thickening agent, so that oil bleeding out of the grease is equivalent to the uninhibited starting liquid in resistance to oxidation, volatilization, and gelation. Essentially similar negative results were obtained with copper phthalocyanine, a diarylurea, sodium terephthalamate, tetrafluoroethylene polymer, and a superfine glass fiber.

THEORETICAL PROBLEMS

The experimental results described raise interesting and urgent questions about the chemistry of the processes leading to an inhibited liquid, the physical state and chemical identity of the inhibitor, the mechanisms by which oxidation and gelation are retarded, and the reasons for the damaging effect of refluxed volatiles on silicone stability. Considerable work has been done on these complex problems and the study is continuing. The results will be reported elsewhere.

LITERATURE CITED

(1) Atkins, D.C., Murphy, C.M., Saunders, C.E., *Ind. Eng. Chem.* **39**, 1395 (1947).
(2) Baker, H.R., Sullivan, F.F., Singleterry, C.R., "Stabilization of Silicone Lubricating Liquids above 200° C. Conventional Oxidation Inhibitors and Some High-Surface Solids," Naval Research Lab., Rept. **5457** (June 2, 1960).
(3) Elliott, J.R., U. S. Patent **2,445,567** (1948).
(4) Federal Test Method Standard **791**, Method 5308.4, "Corrosiveness and Oxidation Stability of Light Oils."
(5) Murphy, C.M., Saunders, C.E., Smith, D.C., *Ind. Eng. Chem.* **42**, 2462 (1950).

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