

are obtained from the ideal energies of vaporization, $\Delta E_i^{\text{ideal}}$, (5),

$$\delta_i = (\Delta E_i^{\text{ideal}}/V_i^0)^{\frac{1}{2}}$$

while the latter are values obtained from measurements of interaction in ternary systems (3, 4). While component pair interactions based upon studies of that isolated binary system are more desirable, this information often is not available. The present procedure was adopted in III and IV because only with hexane is the free energy of mixing hexadecane known.

The greatest known difference among the present systems between the interchange energy obtained from binary system data and that obtained from the ternary studies is found for the hexadecane-hexane pair (1) (-70 and 163 cal. mole⁻¹, respectively). Use of the interchange energy based on binary data produces a maximum change of 0.005 mole-fraction naphthalene solubility from that of the ternary data. This is observed in the hexadecane-hexane-cyclohexane system. A smaller difference, 0.003 mole fraction, is found with the hexadecane-hexane-benzene system. In the first system, the change decreases the agreement between present experimental and predicted solubilities, while in the latter the agreement is improved.

The use in the present study of apparent interaction parameters from measurements in ternary systems lessens the theoretical significance of the results by methods III and IV. The question with which the work is concerned may be reduced to one of whether apparent interaction parameters derived from measurements in ternary systems may be of use in approximate calculations in higher systems.

On theoretical grounds, the assumption of s-regular behavior (Equation 4) in the present systems is more objectionable than is that of regular behavior (Equation 3). In the ternary systems (3, 4), however, there was little difference in the ability of either of the two models to predict behavior. A similar situation exists in the present quaternary systems. A distinction between methods III and IV lies in the fact that the former tends to predict a rather consistently low solubility in the present work.

NOMENCLATURE

V^0 = molar volume
 W = interchange energy, cal. mole⁻¹
 W' = interchange energy, cal. ml.⁻¹
 x = mole fraction
 δ = solubility parameter
 γ = activity coefficient
 ϕ = volume fraction

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Stabilization of Silicone Lubricating Fluids at 300° to 400° C. by Soluble Cerium Complexes

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The discovery that the Si—H bond is involved in the formation of a stable cerium-silicone inhibitor system has been applied to the development of improved methods for stabilizing silicones. The inhibitory process uses initial reactions between hydrous cerous acetylacetonate and a methylhydrogen silicone which proceed and terminate in aerated refluxing benzene to provide a silicone-soluble adduct. The chemistry of the hydride group has been followed quantitatively and some features of structure are postulated for the adduct. Stabilization is completed by aerating a mixture of the cerium adduct and a silicone oil for one hour at 270° to 280° C. There is an optimum concentration of cerium adduct for the stabilization of lightly phenylated dimethyl silicones. The same concentration achieves improvement factors of 100 to 500 in the 300° C. stability of dimethyl silicones and their chlorophenyl- and phenyl-substituted types; with more highly phenyl-substituted silicones, stabilization temperatures are raised to 400° C. and relative improvement factors roughly parallel those observed at 300° C.

IRON, cobalt, nickel, and copper soaps were patented as stabilizers for silicones in 1948 (14). These stabilizers were difficult to solubilize in stable form (12, 13). Solubilization of iron as a silicone-substituted ferrocene has been reported (5, 20, 22).

Other work has demonstrated that a wide range of redox metals inhibited silicones against oxidation, provided the ions were suitably dispersed or solubilized (10). Cerium was chosen for more intensive study because it is commercially available, highly effective, and its stabilizers remain soluble when stabilized silicones are heated in oxygen-poor environments.

The benzene-soluble cerium complex described earlier (7, 10) had the disadvantage of passing into a colloidal precipitate when first added to the silicone. A long processing at 280° C. (with a resulting loss of material and increase in viscosity) is required to remove the volatiles and clarify the stabilized silicone. To obviate these difficulties, a more direct process for the preparation of silicone-soluble cerium compounds was therefore sought.

The discovery that the Si—H bond is involved in the formation of a stable inhibitor system (9) provided a rational approach to the development of improved methods and reactions for stabilizing silicones. The new process improves the

reproducibility of the inhibitor, and raises the stabilization temperature from 325° to 400° C. for several classes of silicones. New oxidation tests have been devised to assess the effectiveness of the stabilization.

EXPERIMENTAL

Commercial Silicones Used. The infrared spectrum of the methylhydrogen silicone (MHS) (15, 16) used in our studies corresponds with the spectrum recently reported by other investigators (23). The refractive index (n_D^{20} 1.3970), average molecular weight (2650), and elemental composition (45.5% Si, 1.59% Si—H Hydrogen), together with the infrared spectrum, show that the MHS has properties corresponding to an average structure $\text{Me}_3\text{Si}(\text{OSiHMe})_{40}\text{OSiMe}_3$. Other commercial silicones used in the present study are characterized in Table I. Each of the silicones is identified by a designation showing the structural type, φ/Me ratio and nominal viscosity.

Synthesis of Cerium Compounds. Tetrakis (trimethylsiloxy) cerium (IV), $\text{Ce}(\text{OSiMe}_3)_4$, ceric acetylacetonate, $\text{Ce}(\text{acac})_4$, and cerous acetylacetonate monohydrate, $\text{Ce}(\text{acac})_3 \cdot \text{H}_2\text{O}$, were prepared and characterized (8). The latter was prepared by a modification of the method of Biltz (11). Precipitation was conducted at a pH of 8.0. The precipitate was dried for 4 days in vacuo, then stored in sealed ampoules.

Inhibitory Process. The cerous acetylacetonate monohydrate (0.082 gram) is converted to normal and basic acetylacetonates in refluxing dry benzene (150 ml.) by passing 200 cc. of dry air per minute through it for 5 to 10 minutes. The resulting solution of $\text{Ce}(\text{acac})_4$ and basic ceric acetylacetonates is combined with 0.125 gram of MHS and refluxed with (dry) aeration (200 cc. per minute) for 1 hour. Stabilization is then completed by rapid heating of the reaction product with the silicone (99.79 grams) to be stabilized to a temperature of 280° C., with continued aeration for 1 hour (8).

Test Methods. Heated-Plate Test (400° C.). This test was developed in the present study as a rapid technique for estimating the stabilization of phenylated silicones at 400° C. The surface temperature of a borosilicate glass sheet ($4 \times 4 \times 1/8$ inch) is maintained at $400^\circ \pm 5^\circ$ C. (Tempilstik crayon) by a standard 7-inch hot plate. About 0.3 gram (15 drops) of the test silicone is placed in the center of the leveled glass sheet, and the time required for gelation is observed. Data show that for the phenylated silicones, the relative stabilities at 300° C. are roughly parallel to those at 400° C.

Thin-Film Test (400° C.). Except for temperature, the procedure duplicates the 300° C. thin-film test described by Baker (10).

Modified-Stagnation Test (400° C.). Twenty grams of the silicone is placed in a borosilicate glass test tube (20×150 mm.) exposed to air in a convection oven adjusted so as to maintain a liquid temperature of either $300^\circ \pm 1^\circ$ C. or $400^\circ \pm 1^\circ$ C. Under these conditions, about 45 mm. of the test tube extends above the liquid level. This test is severe because reactive cyclic and linear decomposition products are not removed by a gas stream but condense on the upper walls of the test vessel and return to the liquid.

RESULTS

Role of Hydride Groups. Earlier work on cerium inhibition of silicone oxidation revealed that the susceptibility of silicones to inhibition paralleled their hydride content, as measured by infrared spectroscopy, and that the "uninhibitable" hydride-free silicones could be inhibited after the addition of a hydride-rich silicone (MHS) (9).

A study of the reactivity of known silicon hydrides revealed that a significant step in the formation of the inhibiting species occurred at moderate temperatures, even though prolonged heating at 280° C. was essential to the total process. In refluxing benzene the Si—H bonds are susceptible to catalyzed hydrolysis ($\equiv\text{SiH} + \text{HOH} \rightarrow \equiv\text{SiOH} + \text{H}_2$) but resistant to oxidation

(17, 21). When the MHS is not diluted by a solvent, the hydrolysis leads to rapid crosslinking by condensation of silanol groups (16), but in dilute benzene solution crosslinking is slow, so that the silanols may react with other OH groups, such as $\equiv\text{CeOH}$. Measurements showed that oxidation of the $\equiv\text{SiH}$ to the silanol ($\equiv\text{SiH} + \text{O} \rightarrow \equiv\text{SiOH}$) (1) becomes appreciable at the boiling point of xylene and goes rapidly at 280° C. The oxidation of MHS (0.1 wt. %) was followed quantitatively (21) in aerated (200 cc. of dry air per minute), refluxing benzene (80° C.), and in aerated, refluxing dry xylene (140° C.).

Choice of Cerium Organic Compounds for Use in the Inhibiting Process. Compounds prepared in connection with the present study include the ceric silanolate, $\text{Ce}(\text{OSiMe}_3)_4$, ceric acetylacetonate, $\text{Ce}(\text{acac})_4$, and cerous acetylacetonate monohydrate, $\text{Ce}(\text{acac})_3 \cdot \text{H}_2\text{O}$. The ceric silanolate, while soluble, was difficult to prepare, store, or handle because of its sensitivity to hydrolysis, and was not studied extensively. Both of the acetylacetonates, however, were silicone-soluble and reactive with MHS to give stable silicone-soluble adducts which produced excellent oxidation inhibition. Both oxygen and a small critical amount of water are required during the low-temperature reaction of cerium acetylacetonates with MHS in the low-temperature stage. The cerous acetylacetonate monohydrate carried, as a stoichiometric component, the optimum amount of water for the reaction. The anhydrous ceric acetylacetonate required separate addition of a somewhat greater amount of water and a more critical control of experimental conditions to give reliable results. The investigation of the low-temperature reaction was therefore carried on largely with $\text{Ce}(\text{acac})_3 \cdot \text{H}_2\text{O}$.

Conditions for the Low-Temperature Step. In the low-temperature step, appropriate molar ratios of $\text{Ce}(\text{acac})_3 \cdot \text{H}_2\text{O}$ and MHS react at high dilutions in aerated refluxing benzene. Only a minor proportion of the $\equiv\text{Si—H}$ groups on a given MHS molecule can be readily reacted to give Ce—O— linkages in refluxing benzene (Figure 1). The slope of the curve in the range of linear relationship corresponds to about 0.8 $\equiv\text{Si—H}$ unit reacted per atom of Ce added. The deviation from 1-to-1 stoichiometry may result either from the uncertainty of the analytical procedures (8, 21) or from the presence of a small proportion of silanols in the starting material. The relationship is valid until about 8 $\text{Ce}(\text{acac})_3 \cdot \text{H}_2\text{O}$ molecules are reacted with 1.0 molecule of MHS (originally containing 40 $\equiv\text{Si—H}$ units). This limited takeup of the Ce by the MHS strongly suggests that steric hindrance prevents further reaction.

Supporting infrared studies on reaction products show in each case that the disappearance of the hydrogen in the $\equiv\text{Si—H}$

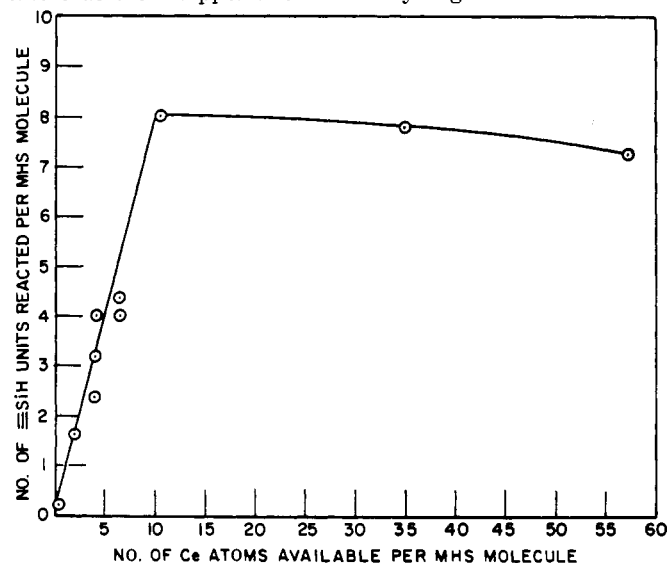


Figure 1. Extent of hydride reaction as a function of the Ce-MHS ratio MHS and $\text{Ce}(\text{acac})_3 \cdot \text{H}_2\text{O}$ in refluxing benzene bubbled with dry air at 200 cc. per minute for one hour.

units is accompanied by the appearance of $\equiv\text{Si}-\text{O}-$ units and the disappearance of about one-third of the coordinated acetylacetonate ligands in the metal chelate.

Completion of the Inhibitory Process at High Temperatures. Stabilization is completed by combining the silicone-soluble MHS adduct with the silicone to be inhibited and submitting the mixture to aeration during a fast and sustained schedule of heating (270° to 280° C., for at least one hour). The stabilized silicone is a sparkling clear orange-yellow liquid exhibiting a weak Tyndall beam and giving a negative test for silane hydrogen. Properties of the starting silicones are summarized in Table I. The stabilized silicones show only small increases in 100° F. viscosity (0.1% to 8.9%) and small losses in weight (0.1 to 3.8%) during processing.

There is firm experimental evidence of the necessity of the heating schedule, aeration, and processing the MHS adduct in the presence of a silicone. A slower and less severe heating schedule leads to systems which carry the cerium ion in a dispersed phase that can be removed by conventional filtration or as a precipitated phase. All attempts to process the low-temperature adduct in nonsilicone solvents to obtain an inhibitor concentrate directly useful in cold silicone oils have failed.

The two-step inhibitory process was optimized with respect to Ce/MHS ratio in the low-temperature step and to final cerium content (wt. %) in the high-temperature step, using lightly phenylated methylphenyl silicones (MPS, 0.05, 50). A Ce/MHS ratio of 3.69 and a cerium concentration of 0.025 wt. % lead consistently to the effective stabilization of the designated silicones, as evidenced by spectacular extensions of gelation times at both 400° and 300° C. If the final cerium concentration is either doubled or halved, gelation time is markedly reduced. The effective 0.025 wt. % cerium concentration of a silicone with a molecular weight of 2600, corresponds to a ratio of one cerium ion to 215 molecules of the silicone.

Particle Size of Inhibiting Entity. A properly stabilized silicone shows little tendency to deposit inhibitor or to lose

stability during one year of storage. The stabilized silicones can be filtered through a 0.1-micron Millipore filter with only minor losses in stabilization.

If $\text{Ce}(\text{acac})_3 \cdot \text{H}_2\text{O}$ is stored in dry air instead of in sealed ampoules before use in the inhibitory process, the particle size of the resulting inhibitor may be as much as 0.8 micron. Stabilization is 20 to 30% less efficient with the larger aggregates. Filtration of stabilized fluids containing the larger aggregates gives water-white fluids having the same low resistance to gelation as the control silicones from which they were prepared.

Inhibition Attainable with Various Kinds of Silicones. The two-stage inhibitory process was also extended without modification to other types of silicones. Principle criteria for estimating the relative effectiveness of the stabilization are the results obtained with the thin-film and modified-stagnation tests at both 300° and 400° C. Results are reported in Table II and Figures 2 to 4.

Increased times to gelation in the 300° C. thin-film tests (Table II) indicate improvement factors ranging from 70 to 475 with several important classes of silicones. The degree of improvement decreases in the order: dimethyl silicones, lightly phenylated methylphenyl silicones, dichlorophenyl-substituted silicones, moderately phenylated methylphenyl silicones, and tetrachlorophenyl-substituted silicones. Except for the tetrachlorophenyl substituted silicone, the order of decreasing improvement parallels the order of increasing stability of the untreated fluids. The various stabilized silicones show greatly suppressed rates of volatilization in the 300° C. thin-film test (Figure 2). Improvement factors in the stagnation tests at 300° C. (Table II) are modest, ranging from 2.5 to 1.0, and are greatest with the dimethyl silicones and their lightly phenylated analogs. In the latter tests, gelation is accompanied by a volatility loss of 20 to 35 wt. %.

The results of thin-film tests at 400° C. (Table II) show that susceptibility to stabilization at this temperature is restricted to the methylphenyl silicones. Lightly and moderately phenylated

Table I. Properties of Silicone Fluids Studied

Designation	Structural Type	n_D^{20}	Approx. ^a Molar Ratio φ/Me	Nominal Viscosity at 25° C. (cs)
DMS	Dimethyl silicone	1.4046	...	50
MPS (0.05,50)	Methylphenyl silicone	1.4274	0.05	50
MPS (0.05,100)	Methylphenyl silicone	1.4256	0.05	100
MPS (0.2,75)	Methylphenyl silicone	1.4587	0.2	75
MPS (medium, 100)	Methylphenyl silicone	1.4838	medium	100
MPS (0.30,100)	Methylphenyl silicone	1.5041	0.30	100
MPS (0.75,300)	Methylphenyl silicone	1.5357	0.75	300
MPS (Cl)(low,50)	Methylphenyl silicone, chlorine Modified	1.4381	low	60
MPS (Cl)(low,80)	Methylphenyl silicone, chlorine Modified	1.4252	low	80

^a Reference (6).

Table II. Response of Various Silicones to Stabilization at 300° and 400° C.

Silicone	300°C.				400°C.				
	Thin-Film Test (Hr. to Gelation)		Stagnation Test (Hr. to Gelation)		Thin-Film Test (Hr. to Gelation)		Stagnation Test (Hr. to Gelation)		
	Inhibited	Control	Inhibited	Control	Inhibited	Control	Inhibited	Control	
DMS	475	1	475	162	65	2.5	0.1	0.1	1
MPS (.05,50)	800	2	400	245	135	1.8	21	0.2	105
MPS (.05,100)	700	2	350	200	135	1.5	15	0.2	75
MPS (.2,75)	1056	7	151	288	216	1.3	66	<0.5	>132
MPS (medium, 100)	1020	14	73	314	314	1.0	42	<0.5	>84
MPS (.30,100)	932	30	31	522	458	1.1	92	1.0	92
MPS (0.75,300)	258	44	5.9	550	440	1.3	20	1.5	13
MPS (Cl)(low,50)	70	1	70	114	90	1.3	2	0.2	10
MPS (Cl)(low,80)	390	1	390	208	165	1.3	17	0.2	85

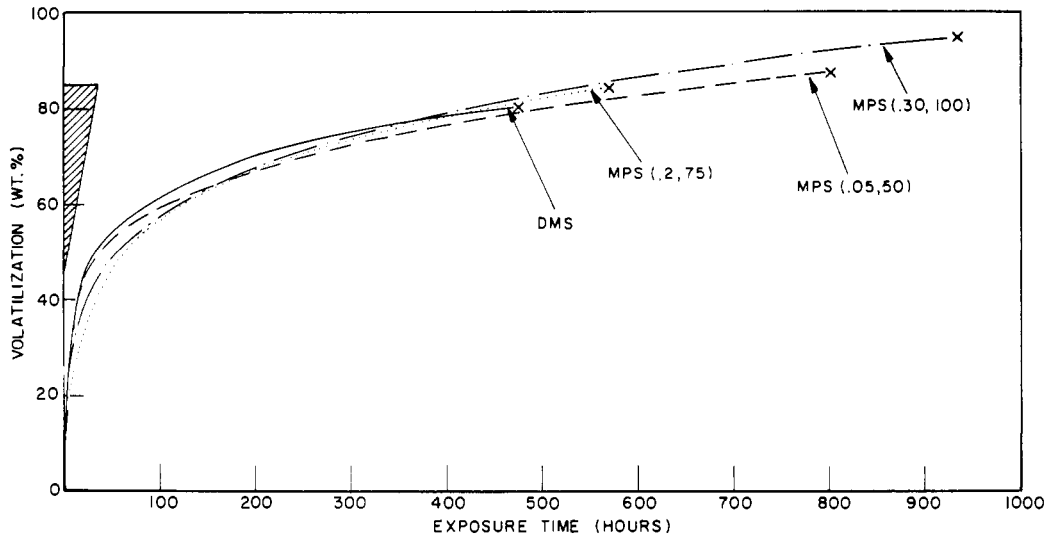


Figure 2. Volatilization loss *vs.* exposure time for typical inhibited silicones in thin-film tests at 300° C. Gelation is denoted by X. Shaded wedge indicates gelation range for controls

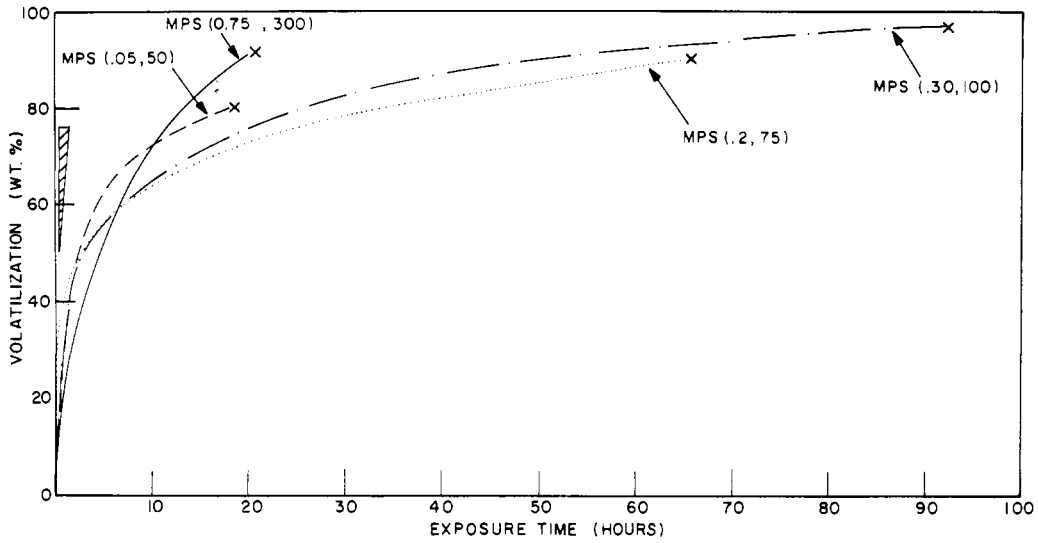


Figure 3. Volatilization loss *vs.* exposure time for typical inhibited silicones in thin-film tests at 400° C. Gelation is denoted by X. Shaded wedge, indicates gelation range for controls

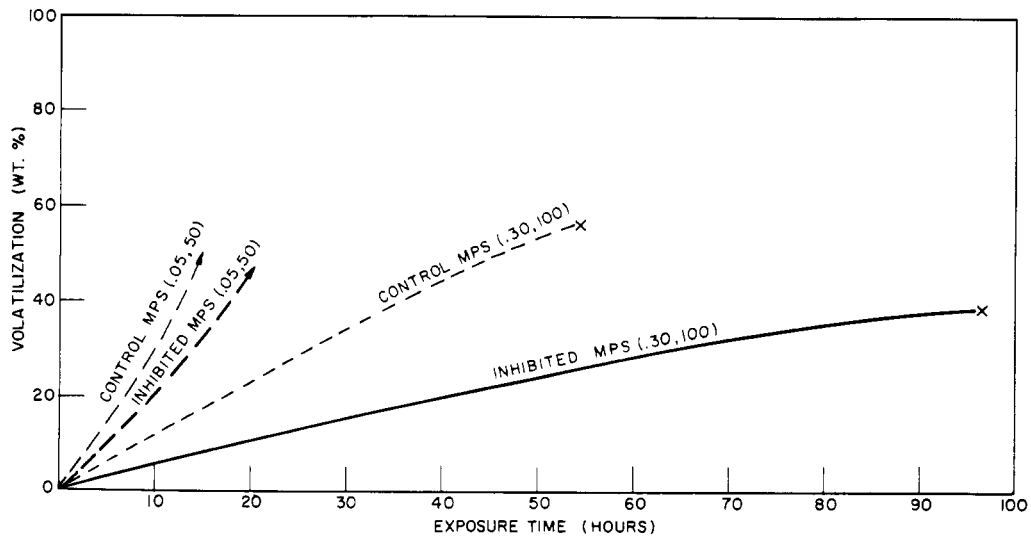


Figure 4. Volatilization loss *vs.* exposure time for control and inhibited silicones in modified stagnation test at 400° C. Gelation is denoted by X. No gelation time noted for control MPS (0.05,50) and inhibited MPS (0.05,50)

methylphenyl silicones give the largest improvement factors amounting to 105 and 132, respectively. The improvement factor for the more highly phenylated silicone is only 13. The times to gelation and the rates of volatilization are shown graphically in Figure 3. The inhibited silicones which volatilize more rapidly in this test show shorter gelation times than do the less rapidly volatilized inhibited silicones.

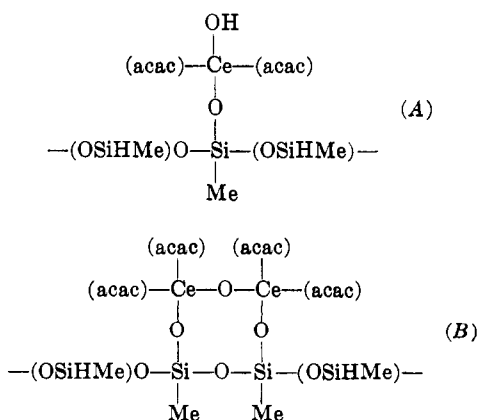
In the 400° C. stagnation test, all of the stabilized silicones resist gelation for 24 hours, but in the case of the lightly phenylated methylphenyl silicones and the MPS(Cl)(low, 80), deep-seated deterioration is indicated by the early appearance (e.g., <6 hours) of a high melting sublimate. With the lightly phenylated methylphenyl silicones, the amorphous crosslinked sublimate analyzes as [(MeSiO_{1.6})_n]. The other moderately and heavily phenylated silicones are satisfactorily stable for 24- and 48-hour periods at 400° C. Volatilization in the 400° C. stagnation test is shown in Figure 4.

Both the reduced volatilization rates and the reduced tendency to form a solid sublimate suggest that cerium stabilization may influence the pyrolytic decomposition at 400° C. Concurrent studies show that the thermal degradation of dimethyl and mixed methylphenyl silicones is drastically reduced by the cerium inhibitor (19). Mechanisms responsible for the stabilization in the absence and presence of oxygen are under study.

DISCUSSION

Chemistry of the Two-Stage Inhibitory Process. Both the physical properties and the complex nature of the MHS-Ce-silicone inhibitor make it difficult to isolate. However, a body of experimental data has accumulated which justifies some inferences about the chemistry of the process by which the inhibiting entity is produced.

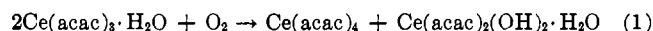
Cerium is reacted chemically with a methylhydrogen silicone in such a way as to give a stable and catalytically active dispersion of submicronic dimensions, and the active site in the MHS is the ≡Si—H group. The cerium acetylacetonate complex reacts with the MHS to eliminate a minor fraction of the silane hydrogen and to give a silicone-soluble adduct with cerium-carrying acetylacetonate ligands. The two basic acetylacetonate residues shown below are considered to satisfy the experimental observation that about one acetylacetonate ligand and one ≡Si—H unit disappear during the binding of one cerium to MHS, and that about one in five of the ≡SiH units reacts.



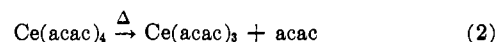
The Stuart-Briegleb model of A suggests that the monomer cerium unit can react with one hydride anion and shield a maximum of three others. If random successive additions of the monomer unit are assumed to occur on the MHS chain, and if it is further assumed that the cerium complex cannot attach to any place where there are less than four adjacent unshielded Si—H groups, calculations show that the ultimate H-Ce ratio will be 4.5. This ratio requires that the intervening unshielded

segments contain an average of 1.5 methylhydrogen siloxy units. Experimentally, the observed H-Ce ratio is 4.2. On this basis, model A satisfies both experimental and geometrical considerations. Similar reasoning with model B shows that the average unshielded segment consists of 2.5 methylhydrogen siloxy units and that the final H-Ce ratio is 3.25. This is substantially smaller than the H-Ce ratio of 4.2 found experimentally.

When dry air is bubbled through a solution of Ce(acac)₃·H₂O in benzene, the resulting dark red solution can be resolved (18) to yield approximately one-half of the cerium as crystalline Ce(acac)₄ and the remainder as a solution of basic ceric acetylacetonate. The main reaction can be written as:

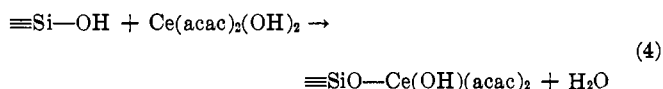


From analogy with Arnett's (2-4, 18) study of Fe(acac)₃, it is considered that Ce(acac)₄ from the above reaction may react as follows:



In turn, the Ce(acac)₃, with the water formed, may be expected to repeat the reaction of Equation 1.

MHS is resistant to oxidation but sensitive to catalyzed hydrolysis at the temperature of refluxing benzene. The reaction between basic ceric acetylacetonate and the hydride group may be formulated alternatively as a preliminary hydrolysis of the hydride to a silanol, followed by elimination of water between the silanol group and the basic cerium compound to give a Ce—O—Si linkage:



or the OH of the basic cerium salt may be postulated to hydrolyze the hydride directly:



Equation 5 is supported by the fact that the number of H₂ molecules evolved closely matches the number of Ce atoms attached to the silicone. Equation 4 suggests that analogous polymeric silanols or silanol-yielding polymers might be substituted for MHS in the stabilization process. This possibility was not investigated.

Silicones are stabilized by aerating a mixture of the low-temperature MHS adduct with the silicone to be inhibited at 280° C. Apparently, the silicones act as a diluent solvent and as a reactant in the high temperature reactions, and the required heating and aeration promote useful reactions between the MHS adduct and the silicone. High-temperature generation of silanol groups can arise from the slow oxidation of methyl groups or the fast oxidation of silane hydrogens usually present in small amount. Aeration at high temperatures readily oxidizes residual silane hydrogen in the MHS to silanols, and at high dilutions in the silicone solvent, these silanol groups either react intermolecularly with ceric acetylacetonate residues attached to MHS chains, condense intramolecularly with themselves to form silsesquioxanes (MeSiO_{1.5})_n, or condense intermolecularly with some of the isolated silanol groups in the silicone molecules. The disappearance of the coordinated acetylacetonate follows from the known sensitivity of such ligands to pyrolysis and hydrolysis. The final result is a stable macromolecule carrying cerium ions in a catalytically active form but otherwise resembling the silicone in which it is dispersed or solubilized.

Experimental evidence indicates that the cerium-bearing inhibitor entity may be present as small macromolecules formed by crosslinking one cerium-MHS molecule with one or several siloxane molecules, as larger crosslinked clusters containing several molecules of each kind, or as colloidal ceric oxide particles a micron or more in diameter. The latter are stabilized by surface linking to silicone or cerium-MHS molecules. Clear dispersions and maximum inhibition are obtained with the smaller units; the procedures for the preparation of the inhibited silicone are dictated largely by the need to secure small inhibitor molecules or aggregates.

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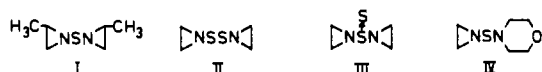
Aziridines. XIV. *N*-Organomercaptoaziridines, a New Class of Aziridine Derivatives

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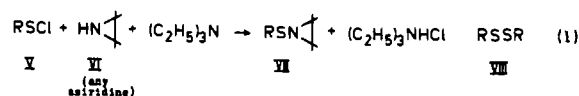
By using five sulfenyl chlorides and three aziridines, 14 *N*-organomercaptoaziridines, representing a new class of aziridine derivatives have been prepared. One of the new compounds, 1-phenylmercaptoaziridine, is effective as a chemosterilant of the screwworm fly.

ONLY A FEW EXAMPLES of aziridine derivatives containing a nitrogen-divalent sulfur bond have been reported in the literature. For example, the reaction of sulfur dichloride with 2-methylaziridine gives the diaziridine sulfide I in poor yield (1). Reaction of ethylenimine with sulfur monochloride, S₂Cl₂, gives a 1,1'-dithiodiaziridine, but it is not clear whether the structure should be represented as II or III (1). The preparation of some mixed aziridine-cyclic secondary amine sulfides, such as IV, has been reported in a German patent (3).



In view of the reports of the biological activity of aziridine derivatives, it appeared desirable to attempt the preparation of some representative examples of the previously unreported class of aziridine derivatives, the *N*-organomercaptoaziridines

VII, for testing as insect chemosterilants. The desired preparation was readily accomplished by addition of an organosulfenyl halide V to a solution of an aziridine VI in an inert solvent in the presence of triethylamine, according to Equation 1. In this way, 14 different organomercaptoaziridines were prepared, using five different halides and the three aziridines, ethylenimine, 2-methylaziridine, and cyclohexenimine. The products were isolated in satisfactory yields of 50-98%. A disulfide, VIII, was sometimes formed in small yield as a by-product in the preparation.



The phenyl, *p*-chlorophenyl, *p*-bromophenyl, and trichloromethylmercaptoaziridines were isolated as colorless liquids having a persistent, characteristic odor. They were sufficiently stable to heat to permit purification by vacuum distillation at