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

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The Si-H bond has been shown to be involved in the formation of a stable cerium-silicone inhibitor system and this discovery has been applied to the development of improved methods for stabilizing silicones. The inhibitory process uses initial reactions between hydrous cerous acetylacetonate and a polymethylhydrogen silicone. These reactions 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. The simplified inhibitory process is a two-step reaction. 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 100 to 500 percent improvements 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.

INTRODUCTION

Iron, cobalt, nickel, and copper soaps were cited and patented as stabilizers for silicones in 1948 (1). These stabilizers were difficult to solubilize in stable form, and they were not brought into use until nearly ten years later (2-4).

Work conducted by this laboratory between 1952 and 1959 demonstrated that a wide range of redox metal ions inhibited silicones against oxidation, provided the ions were suitably dispersed or solubilized. It was shown that when disalicylalpropylenediamine was used as an intermediate reagent that metal ions could be dispersed in silicones in extraordinarily stable and active states (5-7). Our studies confirmed the effectiveness of copper and iron ions and revealed that certain rare earth ions (e.g., cerium, praseodymium, and europium) were also effective oxidation inhibitors.

Of the redox metals showing promise in our early inhibitory process, cerium was chosen for more intensive study. It is commercially available, highly effective, and not reduced to insoluble products when heated in oxygen-poor environments. It is recognized that an intensive study of

copper and iron compounds might lead to stabilities comparable to that obtained with cerium. Other investigators have reported the use of a silicone-substituted ferrocene which gave a stable and effective inhibitor for silicone liquids (4,8-10).

The commercial applicability of the original inhibitory process developed at this laboratory has several limitations. Processing for 12 to 72 hours by aeration at 285°C is required to remove volatile products and clarify the stabilized silicone. In many cases stabilization is accompanied by 20 to 30 percent weight losses and 20 to 30 percent increases in viscosity. The inhibitory process fails with two classes of improved-lubricity silicones and some samples of dimethyl silicones. Stability is erratic at temperatures above 325°C.

The necessity for long periods of processing at high temperatures was associated with the formation and resolution of a massive colloidal precipitate in order to obtain cerium ion in a stable dispersed phase. To obviate such difficulties, other reactions between cerium compounds and silicones were sought that could proceed and terminate in the liquid phase. If such reactions could be found, it was reasoned that the energy requirements for stabilization could be reduced, some of the reactions could be followed, and variables controlling the size and efficiency of the inhibiting entity could be studied.

NRL Problems C02-02 and C02-12; Projects NR Task RR 007-08-44-5500 and NR Task RR 001-01-43-4752. This is an interim report; work on this problem is continuing. Manuscript submitted July 27, 1964.

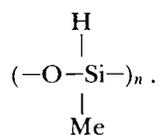
The discovery that the Si-H bond is involved in the formation of a stable inhibitor system is applied to the development of improved methods and reactions for stabilizing silicones. The new inhibitory process reduces the time and energy requirements for stabilization, improves the effectiveness and reproducibility of the inhibitor, and raises the stabilization temperature from 325° to 400°C for several classes of silicones. Also new oxidation tests have been developed for estimating silicone stabilization at 300° and 400°C.

Other areas of study dealing with this discovery include properties of promising reactants for the stabilization of silicones, the quantitative study of low- and high-temperature stages in the inhibitory process, and the reactant ratios for optimizing the stabilization. Some structural features are postulated for the low-temperature adduct and the stabilized inhibitor.

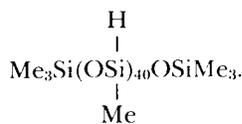
EXPERIMENTAL MATERIALS

Commercial Silicones Used

Other investigators (11-13) have identified DC 1107 as a methylhydrogen silicone (MHS) resembling liquid dimethyl silicones but containing the repeating polymeric units



The infrared spectrum (Table 1) of the DC 1107 used in our studies corresponds with the one recently reported by other investigators (13). The refractive index, average molecular weight, and elemental composition of this MHS are given in Table 2. The tabulated data show that the MHS has properties corresponding to an average structure



Other commercial silicones used in the present study are identified by the manufacturer's code,

TABLE I
Infrared Spectrum of DC 1107

| Wavelength (μ) | Interpretation* |
|--|---|
| 3.37 (w) | C-H stretching of CH ₃ group |
| 4.62 (s) | Si-H stretching |
| 7.10 (w) | C-H bending of CH ₃ group (antisymmetric) |
| 7.94 (s) | C-H bending of CH ₃ group (symmetric) |
| 9.13 and 9.53 (vs) } | Si-O and Si-O-Si stretching modes |
| 10.85 (m, sh) | Si-H bending mode |
| 11.25 (vs) } 11.93 (vs) } 13.03 (vs) } | Si-CH ₃ rocking and Si-C stretching modes |

*Assignments are the same as those reported† except for the band at 7.94 which was attributed by the other investigators to a Si-CH₃ rocking vibration.

†I. Shihari, W. Kawai, and T. Ichihashi, *J. of Polymer Sci.* **57**:837 (1962).

by structural designation, refractive index, approximate degree of phenylation (14), and nominal viscosity at 25°C (Table 3). The various commercial silicones were used as received unless specified otherwise.

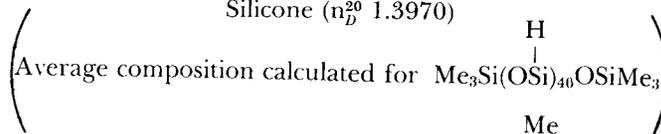
Synthesis of Cerium Compounds

Tetrakis (trimethylsiloxy) Cerium (IV) — Two intermediates required for this synthesis were prepared by published procedures. The trimethylacetoxysilane (bp 28°C/30 mm Hg) was prepared by the method of Schuyten (15). Solvated ceric isopropoxide [Ce(OPr-iso)₄·Pr-isoOH] was prepared by Bradley's method (16,17). To avoid undesirable side reactions in the transesterification reaction to be undertaken, the solvated ceric isopropoxide was converted to solvent-free ceric isopropoxide. The conversion of the solvate to the desired compound by freeze-drying techniques had been observed in our earlier studies. Just before use, the solvated ceric isopropoxide (20.00 g, 0.0458 mole) was freeze-dried in 100 ml of benzene to give 17.24 g of product as a yellow amorphous solid.

Analysis calculated for Ce(OPr-iso)₄: Ce, 37.22; OPr-iso, 62.78.

Found: Ce, 37.0; OPr-iso, 62.3.

TABLE 2
Characterization of DC 1107 Methylhydrogen
Silicone (n_D^{20} 1.3970)



| | Molecular Weight | Si (%) | Si-H Hydrogen (%) |
|------------|------------------|--------|-------------------|
| Calculated | 2567.5 | 45.95 | 1.57 |
| Found | 2560 | 45.5 | 1.59 |

TABLE 3
Properties of Silicone Fluids Studied

| Type | Designation | n_D^{20} | Approx.* Molar Ratio ϕ/Me | Nominal Viscosity at 25°C(cs) |
|-----------------------|--|------------|---|-------------------------------------|
| DC 200 | Dimethylsilicone | 1.4046 | | 50 |
| DC 510 | Methylphenylsilicone | 1.4274 | 0.05 | 50 |
| DC 510 pot residue A† | Methylphenylsilicone | 1.4320 | 0.05 | 60 |
| DC 510 pot residue B‡ | Methylphenylsilicone | 1.4257 | 0.05 | 70 |
| DC 510 | Methylphenylsilicone | 1.4256 | 0.05 | 100 |
| XF-258 | Methylphenylsilicone | 1.4587 | 0.2 | 75 |
| XF-258 pot residue§ | Methylphenylsilicone | 1.4611 | 0.2 | 100 |
| SF-1017 | Methylphenylsilicone | 1.4838 | | 100 |
| DC-550 | Methylphenylsilicone | 1.5041 | 0.35 | 100 |
| DC-710 | Methylphenylsilicone | 1.5357 | high | 300 |
| DC F-60 | Methylphenylsilicone, chlorine modified | 1.4381 | low | 60 |
| GE F-50 | Methylphenylsilicone, chlorine modified | 1.4252 | low | 80 |

*R.C. Gunderson and A.W. Hart, eds., "Synthetic Lubricants," New York:Reinhold, pp. 275, 278, 279, and 3.16, 1962.

†Residue after stripping 30% of the DC 510 liquid in a molecular still at 200°C and 10 microns pressure (H.R. Baker and C.R. Singleterry, NRL Report 5474, Aug. 12, 1960).

‡A similar residue H.R. Baker and C.R. Singleterry, *J. Chem. Eng. Data* 6:146 (1961).

§Residue after stripping 30% of the XF-258 liquid in a molecular still.

The transesterification method of Bradley and Thomas (18) for preparing corresponding titanium derivatives was adapted to the preparation of tetrakis (trimethylsiloxy) Ce(IV). A mixture of trimethylacetoxysilane (17.16 g; 0.1298 mole) in cyclohexane (100 ml) was added slowly over a 3-1/2 hour period to a refluxing mixture of ceric isopropoxide (12.21 g; 0.03243 mole)

in cyclohexane (500 ml). The isopropyl acetate that formed was distilled azeotropically through an efficient column. Removal of the azeotrope was followed by refractive index measurements and shown to be completed in 16 hours. Saponification of the distillate indicated that more than 96% of the ester had distilled. The residual mixture was concentrated at reduced pressure

and finally freeze-dried in 30 ml of benzene to yield 16.27 g (100% yield) of product as a dull yellow solid that pulverized like camphor.

Analysis calculated for $Ce(C_3H_9SiO)_4$: Ce, 28.20; Si, 22.60.

Found: Ce, 27.95; Si, 22.42.

Moisture must be rigorously excluded from each stage of the synthesis and from the stored product.

Ceric Acetylacetonate [$Ce(acac)_4$] — Dry ammonia (200 cc/min) was bubbled through a mixture of acetylacetonone (50.0 g, 0.50 mole), benzene (1500 ml), and ethyl alcohol (50 ml), while a mixture of ceric ammonium nitrate (54.8 g, 0.10 mole) and dry ethyl alcohol (150 ml) was added over a period of 10 minutes. Addition of ammonia was continued for another 20 minutes. Then the reaction mixture was bubbled with dry air for 20 minutes. Insoluble salts that formed were removed by centrifugation. Solvent from the supernatant was removed in vacuo, and the resulting residue was redissolved in benzene, filtered, concentrated, and recrystallized three times from 1500 ml of boiling heptane yielding 16.1 g (30% yield) of product as black crystals; mp 160°-161°C.

Analysis calculated for $Ce(C_5H_7O_2)_4$: Ce, 26.12; C, 44.77; H, 5.26.

Found: Ce, 26.36; C, 44.63; H, 6.22.

Molecular Weight (calculated) 536.6; molecular weight (found) 533.

To prevent hydrolysis, water must be excluded from the stored product.

Cerous Acetylacetonate Hydrate [$Ce(acac)_3 \cdot H_2O$] — This compound was prepared by a modification of the method by Biltz (19). Acetylacetonone (100.0 g, 1.00 mole) was dissolved in a mixture of water (100 ml) and 15N ammonium hydroxide solution (45 ml). The resulting mixture was added during 10 minutes to a stirred mixture of cerous nitrate hexahydrate (100 g, 0.231 mole) and water (300 ml). The resulting clear orange solution was stirred as 7.5N ammonium hydroxide solution (40 ml) was added during 10 minutes to precipitate a hydrous yellow product at a final pH of 8.0. The precipitate was washed repeatedly with ice water containing a small amount of acetylacetonone (eight 100 ml washes), then washed with petroleum ether, and finally

dried for 4 days at 0.5 mm Hg to yield 101 g (96% yield) of yellow amorphous crystals; mp 140-142°C. The yellow product on exposure to dry air gradually turns light brown in color. To prevent oxidation, samples of the yellow product are stored in glass ampoules which are evacuated and sealed.

Analysis calculated for $Ce(C_5H_7O_2)_3 \cdot H_2O$: Ce, 30.77; C, 39.55; H, 5.98; N, 0.00.

Found: Ce, 30.71; C, 39.50; H, 5.40; N, 0.00.

Infrared Spectra of Cerium Acetylacetonates — Infrared spectra of $Ce(acac)_4$ and $Ce(acac)_3 \cdot H_2O$ were obtained with a Perkin-Elmer spectrometer by incorporating the chelates in KBr disks. These spectra (Table 4) possess all the absorption bands observed by Lecomte (20) for a wide variety of metal acetylacetonates. Agreements with reported frequencies are excellent and there is no reason to question the proposed structures of the compounds. As expected, the cerous chelate has a weak absorption band in the 3-micron region which is undoubtedly due to the water of hydration.

EXPERIMENTAL PROCEDURES

Analytical Methods

Cerium — The percent cerium in organic cerium compounds was determined by ignition to ceric oxide CeO_2 .

Silicon — The percent silicon was determined by standard wet oxidation procedures with sulfuric acid, followed by evaporation of volatile materials and ignition of the residue to SiO_2 . In the case of $Ce(OSiMe_3)_4$ the wet oxidation was conducted in a closed system to assure complete oxidation of volatile hydrolytic intermediates. Subsequent evaporation and ignition left a residue of SiO_2 and CeO_2 . Removal of SiO_2 with aqueous 48% hydrofluoric acid left a residue of CeO_2 from which the SiO_2 was calculated by difference.

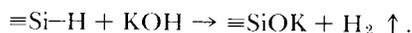
Isopropoxy content — This was determined by oxidation with excess chromic acid (sulfuric acid and potassium dichromate), followed by addition of potassium iodide and titration of the iodine released with standard thiosulfate making appropriate corrections for the reduction of Ce(IV) to Ce(III) by iodine (17).

TABLE 4
Observed Infrared Spectra
of Cerium Acetylacetonates

| Mode* | Ce(acac) ₃ ·H ₂ O | Ce(acac) ₄ |
|--|---|-----------------------|
| (12)ν(C=O) _{as} | 1596 (vs) | 1584 |
| (11)ν(C=C) | 1511 (vs) | 1520 |
| (10) (CH ₂ or CH ₃) | 1440 (w) | 1425 |
| (9)ν(C=O) s. | 1380 (vs) | 1389 |
| (8) CH ₂ or CH ₃ | 1350 (w) | 1363 |
| | 1255 (s) | 1351 |
| | | 1261 |
| (7)ω ₄ (C-C) | 1185 (w) | 1185 |
| (6) (CH ₂ or CH ₃) | 1012 (m) | 1015 |
| (5) (CH ₂ or CH ₃) | 915 (m) | 941 |
| | | 922 |
| (4)ω ₁ (C-C) | 759 (m) | 775 |
| | | 759 |
| | 632 | 653 |
| (3)ω ₃ -(C-C) | 522 | 531 |
| (1)ω ₆ -(C-C) | 398 | 401 |
| | 322 | 323 |

*Taken from J. Lecomte, *Disc. Faraday Soc.* No. 9:125 (1950).

Total silane hydrogen, H(-Si≡)—The percent silane hydrogen in MHS was determined by measuring the hydrogen evolved by the action of 1N ethanolic potassium hydroxide in a modified Zerewitinoff apparatus (21). This method has been used successfully in measuring the silane hydrogen of low molecular weight methylhydrogen siloxanes (21), employing the following stoichiometric relationship:



Molecular weights—Molecular weights were determined in a Mechrolab Vapor Pressure Osmometer, Model 30, calibrated with benzene solutions of benzil.

Inhibitory Process, Low-Temperature Stage

Adduct (A)—Water (0.08 g) is dissolved in dry benzene (300 ml) preferably by supersonic agitation.

To this mixture successive additions of Ce(acac)₄ (0.100 g) and MHS (0.125 g) are made, using small amounts of benzene for the transfers. The reaction mixture is refluxed and aerated (200 cc dry air/min) for 1 hour, then concentrated to 100 ml by the removal of solvent.

Adduct (B)—The disproportionation of Ce(acac)₃·H₂O is accomplished by refluxing and aerating (200 cc dry air/min) a mixture of dry benzene (150 ml) and Ce(acac)₃·H₂O, (0.082 g) for 5 to 10 minutes. Then MHS (0.125 g), dissolved in a small amount of dry benzene, is added and the resulting mixture is refluxed and aerated for 1 hour.

Concentrate (C)—A concentrate of adduct (B) can be prepared by adding 10 g of the silicone to be inhibited, removing the solvent at reduced pressure, and taking precautions to exclude moisture. The single phase concentrate should be used immediately in the next step.

Inhibitory Process, High-Temperature Stage

Adducts (A) or (B) or the concentrate (C) are combined with sufficient silicone to total a 100 g mixture, exclusive of solvent benzene. This mixture is aerated (200 cc dry air/min) and heated so that the liquid temperature reaches 270° to 280°C in 7 to 10 minutes. Aeration at 270°C is continued for 1 hour to give stabilized silicones, which appear as clear orange-yellow liquids exhibiting a weak Tyndall beam.

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" × 4" × 1/8") is maintained at 400° ± 5°C by a standard 7 inch hot plate. About 0.3 g (15 drops) of the test silicone is placed in the center of glass sheet. The hot plate is then levelled with small wedges to keep the silicone on the plate in a large puddle, and the time required for gelation is observed. Data show that the relative stability at 300°C is roughly parallel to that at 400°C.

Thin-Film Test (400°C)—In this test 0.50 g of silicone is heated in an open borosilicate Petri

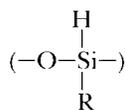
dish (60 mm × 15 mm) in a convection oven at 400°C. Volatile losses are followed by periodic weighing and the time to gelation noted. Except for temperature, the procedure duplicates the 300°C thin-film test described by Baker (7).

Modified-Stagnation Test (400°C)—This test is similar to the previously described test conducted in short-form test tubes (7) except that a smaller amount of material is condensed and returned. Twenty grams of the silicone is placed in a borosilicate test tube (20 mm × 150 mm) exposed to air in a convection oven and maintained at a liquid temperature of either 300° ± 1 or 400° ± 1°C. Under these conditions about 45 mm of the test tube extends above the liquid level.

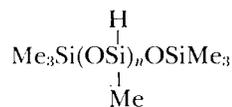
RESULTS

Necessity for Hydride Groups

Earlier work on cerium inhibition of silicone oxidation showed a wide variation in the susceptibility of commercial silicones to inhibition by the published procedure (7). These differences occurred between dimethyl silicones of similar viscosity from different producers. It was also found that inhibitable silicones became uninhibitable after refluxing with methanol. Inhibited silicones from which the inhibitor had been removed by a 0.3 μ filter could not be reinhibited by repeating the original treatment. These anomalies were cleared up by the discovery that susceptibility to inhibition paralleled the hydride



content of the silicone as measured by infrared spectroscopy. Hydrides occur in small amounts in most but not all commercial silicone liquids; the hydride group is destroyed in refluxing methanol and by the processing with cerium which yields an oxidation-inhibited silicone. The simple absence of hydride from the silicone, however, did not lead to better oxidation stability. It was further shown that the "uninhibitable" hydride-free silicones could be inhibited after the addition of a hydride-rich silicone, e.g.,

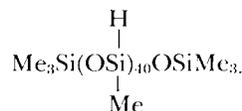


(MHS, Ref. 22).

The availability of the reactive silicone species in concentrated form prompted a study of the chemical reactions involved in the preparation of inhibited silicones. It was found that the order of mixing reactants at room temperature affected the final inhibition. This observation indicated 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. This discovery led to a superior inhibition procedure involving quite distinct low-temperature and high-temperature steps. The low-temperature step involved the reaction of a cerium-containing intermediate with the hydride alone; a much shortened high-temperature step incorporated the cerium-MHS compound in a large volume of the silicone to yield a stable dispersion or solution with superior oxidation resistance.

Properties of Methyl Hydrogen Silicone (MHS) Pertinent to the Stabilization Studies

On the basis of infrared spectra and the data in Tables 1 and 2, it is concluded that the MHS used has an average structure corresponding to



In refluxing benzene the $\equiv\text{Si}-\text{H}$ bonds are susceptible to catalyzed hydrolysis ($\equiv\text{SiH} + \text{H}_2\text{O} \rightarrow \equiv\text{SiOH} + \text{H}_2$) but resistant to oxidation (23). When the MHS is not diluted by a solvent, the hydrolysis leads to rapid crosslinking by condensation of the silanol groups with elimination of water (23), but in dilute benzene solution crosslinking is slow, so that the silanols may react with other OH groups, such as $\equiv\text{CeOH}$. Oxidation of the $\equiv\text{SiH}$ to the silanol ($\equiv\text{SiH} + \text{O} \rightarrow \equiv\text{SiOH}$) (24) becomes appreciable at the boiling point of xylene and goes rapidly at 280°C.

The oxidation of MHS (0.1 wt %) was followed quantitatively in aerated (200 cc dry air/min)

refluxing dry benzene (80°C) and in aerated refluxing dry xylene (140°C). The stability of MHS against oxidation in refluxing benzene was evidenced by the small decrease (<0.5%) in the silane hydrogen content observed after 1 and 4 hours of reaction time. At the higher temperature of refluxing xylene, the MHS showed a 5.0% decrease in silane hydrogen after 1 hour of reaction.

Choice of Cerium Organic Compounds for Use in the Inhibiting Process

The cerium compound used in the original inhibition procedures was a benzene-soluble reaction product of ceric toluate and disilylpropylenediamine (DSPD). Although it gave excellent results, it had the disadvantage of passing into a colloidal precipitate when first added to the silicone. A long processing at 280°C was required to clear this precipitate; in unfavorable circumstances it was never completely dissolved but converted in part to a yellow cerium-containing precipitate which settled out on standing. Silicone-soluble cerium compounds were therefore sought as starting materials for inhibition work.

Low-temperature reactions leading to basic and normal cerium toluate soaps, and their reactions with DSPD are described elsewhere (17,25). Compounds prepared in connection with the present study include the cerium 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. Its synthesis was of interest in demonstrating the possibility of the $\text{Ce}-\text{O}-\text{Si}\equiv$ bond. Both of the acetylacetonates, however, were found to be silicone soluble and reactive with MHS to give silicone-soluble adducts which, when heated with commercial silicones oils at 280°C with a supply of air, gave stable solutions and excellent oxidation inhibition.

Experiment showed that a small critical amount of water was 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 $\text{Ce}(\text{acac})_3 \cdot \text{H}_2\text{O}$. Separate experiments showed that the reactions with $\text{Ce}(\text{acac})_4$ followed the same general pattern. Briefly, the cerous acetylacetonate is converted to normal and bases ceric acetylacetonates in refluxing benzene by passing a stream of dry air through it for 5 to 10 minutes. The resulting solution of $\text{Ce}(\text{acac})_4$ and basic ceric acetylacetonates is combined with appropriate amount of MHS and refluxed with (dry) aeration, for 1 hour. Stabilization may then be completed by rapid heating of the reaction product with the silicone to be stabilized to a temperature of 280°C for 1 hour. (Alternatively, the low-temperature reaction product may be diluted with a moderate amount of the silicone liquid and the benzene removed at a low temperature to yield a silicone concentrate of the intermediate which can be stored for later use. Extended storage is not recommended.)

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. Under these conditions homogeneity is maintained, and the reaction is substantially complete after 1 hour. If comparable reactions are conducted in refluxing xylene, undesirable side reactions lead to the precipitation of 20 to 30 wt % of the cerium as basic acetylacetonates.

It appears that only a minor proportion of the $\equiv\text{Si}-\text{H}$ groups on a given MHS molecule can be readily reacted to given $\text{Ce}-\text{O}$ -linkages in refluxing benzene. The results are presented graphically in Fig. 1, where the number of $\equiv\text{Si}-\text{H}$ units (*i.e.*, hydride anions) consumed per MHS molecule is plotted against the number of Ce atoms reacted per MHS molecule. The slope of the curve in the range of linear relationship corresponds to about 0.8 $\equiv\text{Si}-\text{H}$ unit reacted per atom of Ce added, *i.e.*, to 0.8 mole of hydrogen evolved for each atom of Ce added. 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

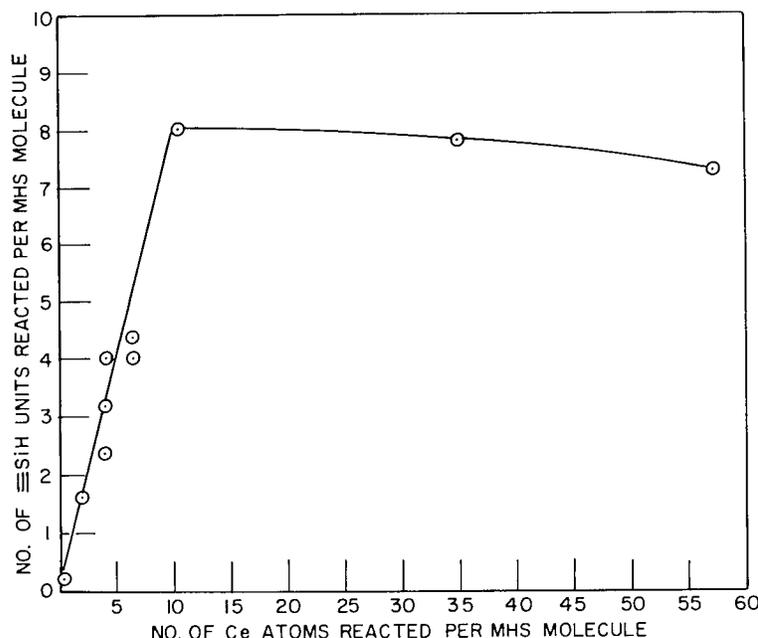


Fig. 1 - Extent of hydride reaction as a function of the Ce/MHS ratio [MHS and $\text{Ce}(\text{acac})_3 \cdot \text{H}_2\text{O}$ in refluxing benzene bubbled with dry air at 200 cc/min for one hour]

containing $40 \equiv \text{Si}-\text{H}$ units). Further consumption of $\equiv \text{Si}-\text{H}$ units is not observed even when large excess quantities of $\text{Ce}(\text{acac})_3 \cdot \text{H}_2\text{O}$ are added. This limited takeup of the Ce by the MHS strongly suggests the possibility that steric hindrance prevents further reaction.

Supporting infrared studies on reaction products (obtained using Ce/MHS ratios of 3.7 and 6.7) show in each case that the disappearance of the hydride anions in the $\equiv \text{Si}-\text{H}$ 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. A concentrate of either reaction product, when examined in a KBr disk, showed a decrease in the intensity of the $\equiv \text{Si}-\text{H}$ bands at 4.62μ and 11.93μ relative to the $\text{Si}-\text{O}-$ peak at 9.13μ . Bands due to cerium acetylacetonate (e.g., 6.25μ) also decreased in relation to the 9.13μ band. Quantitative estimates could be made from these measurements.

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 appears as a sparkling clear orange-yellow liquid exhibiting a weak Tyndall beam and giving a negative test for silane hydrogen. Properties of the starting silicones (i.e., control silicones) are summarized in Table 3. As a result of the processing, the stabilized silicones show small increases in 100°F viscosity (0.1% to 8.9%) and small losses in weight (0.1% to 3.8%).

The necessity for the heating schedule, for aeration and for processing the MHS adduct in the presence of a silicone is firmly established experimentally. A slower and less severe heating schedule leads to systems which carry the cerium ion in a heterogeneous phase (i.e., in a dispersed phase which can be removed by conventional filtration or as a precipitated phase). Finally all attempts to process the low-temperature adduct in nonsilicone solvents to obtain a useful inhibitor concentrate have failed.

Optimization of Cerium Content

The two-step inhibitory process was optimized with respect to Ce/MHS ratio in the low-temperature step and to cerium content (wt %) in

the high-temperature step, using DC 510 silicones as identified in Table 3. A systematic study of this problem required the development of the 400°C heated-plate test to estimate the stabilization at 400° and 300°C. The effectiveness of the stabilization was usually confirmed by thin-film tests and by modified-stagnation tests (at both 300° and 400°C). A description of each of these methods is given in the Experimental Section.

The two-step inhibitory process was studied in some detail using $\text{Ce}(\text{acac})_4$, MHS, and H_2O as reactants for the low-temperature reaction. The results in Table 5 demonstrate the necessity for adding critical amounts of water to obtain stabilized silicones carrying all the cerium in a stable soluble or dispersed phase. In the highly dispersed systems, the silicone stabilization is improved by reducing the cerium concentration from 0.052 wt % to 0.026 wt %.

The two-step inhibitory process has been studied intensively using $\text{Ce}(\text{acac})_3 \cdot \text{H}_2\text{O}$ and MHS as

intermediates in the stabilization of DC 510 silicones. This preferred system avoids the problem of adding water in the low-temperature stage and maintains the homogeneity required for optimizing the stabilization. Effects of Ce/MHS ratios for the first step and of Ce concentration for the second step are given in Table 6. These results show that a Ce/MHS ratio of 3.69 and a cerium concentration of 0.025 wt % lead consistently to the effective stabilization of the DC 510 silicones, as evidenced by spectacular extensions of gelation times at both 400° and 300°C. If the same Ce/MHS ratio is employed, but the cerium concentration is either doubled or halved, gelation time is markedly reduced. In the case of a DC 510 silicone with a molecular weight of 2600, the effective 0.025 wt % cerium concentration corresponds to a ratio of one cerium ion to 215 molecules of the DC 510 silicone.

The less critical sensitivity of the DC 510 pot residue B to different Ce/MHS ratios (see Table 6,

TABLE 5
Effects of Cerium Concentration on the Stabilization*
of DC 510 Silicones Using MHS, $\text{Ce}(\text{acac})_4$, and H_2O

| Run No. | Test Silicone | H_2O Added† (wt %) | Molar Ratio $\text{Ce}(\text{acac})_4$ MHS | Cerium Conc. in Processed Silicone (wt %) | Time to Gelation (hrs) | |
|---------|-------------------------|--|--|---|------------------------------|---------------------------|
| | | | | | Heated-Plate Test (400°C) | Thin-Film Test (300°C) |
| Control | DC 510 (50) | 0.00 | none | none | 0.1 | 2.0 |
| 1 | DC 510 (50) | 0.00 | 3.83 | 0.052‡ | 1.2 | 576.0 |
| 2 | DC 510 (50) | 0.08 | 3.83 | 0.052§ | 1.0 | 240.0 |
| 3 | DC 510 (50) | 0.08 | 3.83 | 0.026§ | 4.0 | 750.0 |
| Control | DC 510 Pot Residue B | 0.00 | none | none | 0.1 | 2.0 |
| 4 | DC 510 Pot Residue B | 0.08 | 3.83 | 0.026§ | 4.2 | 670.0 |
| 5 | DC 510 Pot Residue B | 0.04 | 6.67 | 0.026‡ | 0.2 | 72.0 |
| 6 | DC 510 Pot Residue B | 0.08 | 6.67 | 0.026§ | 4.0 | 700.0 |

*Stabilization by the two-stage inhibitory process.

†Water dissolved in benzene and added to the low-temperature stage of reaction.

‡Milky or turbid fluid that deposits part of the cerium as a precipitate.

§All of the cerium is held in a stable soluble or dispersed phase.

TABLE 6
Effects of Cerium Concentration on the Stabilization*
of DC 510 Silicones Using MHS and $\text{Ce}(\text{acac})_3 \cdot \text{H}_2\text{O}$

| Run No. | Test Silicone | Molar Ratio $\text{Ce}(\text{acac})_3 \cdot \text{H}_2\text{O}$ MHS | Cerium Conc. in Processed Silicone (wt %) | Time to Gelation (hrs) | | |
|---------|-------------------------|---|---|------------------------------|---------------------------|---------------------------|
| | | | | Heated Plate Test (400°C) | Thin Film Test (400°C) | Thin Film Test (300°C) |
| Control | DC 510 (50) | none | none | 0.1 | 0.2 | 2.0 |
| 7 | DC 510 (50) | 3.69 | 0.025 | 4.0-4.5 | 18-21 | 700-800† |
| 8 | DC 510 (50) | 3.69 | 0.050 | 1.2 | — | 264 |
| 9 | DC 510 (50) | 6.59 | 0.025 | 0.2 | — | 72 |
| Control | DC 510 Pot Residue A | none | none | 0.1 | 0.2 | 2.0 |
| 10 | Residue A | 3.69 | 0.025 | 6.0 | 18.0 | 800 |
| 11 | Residue A | 3.69 | 0.050‡ | 3.5 | — | 408 |
| Control | DC 510 Pot Residue B | none | none | 0.1 | 0.2 | 2.0 |
| 12 | Residue B | 3.69 | 0.012 | 0.1 | — | 360 |
| 13 | Residue B | 3.69 | 0.025 | 4.2 | — | 800 |
| 14 | Residue B | 3.69 | 0.050 | 1.0 | — | 168 |
| 15 | Residue B | 4.96 | 0.025 | 3.5 | — | 720 |
| 16 | Residue B | 6.59 | 0.025 | 5.0 | 3.0 | 792 |
| 17 | Residue B | 9.95 | 0.025‡ | 0.2 | — | 200 |
| Control | DC 510 (100) | none | none | 0.1 | 0.2 | 2.0 |
| 18 | DC 510 (100) | 3.69 | 0.025 | 4.2 | 18.0 | 700 |

*Stabilization accomplished by the two-stage inhibitory process.

†Data obtained on silicones stabilized in a number of experiments.

‡Processed silicone is a hazy mixture that slowly deposits cerium-containing complexes.

Runs 12-17) may be due to inherent differences in the various DC 510 silicones, but it appears more likely that the observed differences are due to previous overheating during the stripping of the silicone in a molecular still. Oxidation products (gelling) were observed on the molecular still rotor after stripping at 200°C and 10 microns pressure. Such incipient oxidation would be expected to lead to more Si—OH groups which could compete more effectively for involvement with the low-temperature MHS adduct in

the second step of the stabilization. Our failure to obtain a higher degree of stabilization at 400°C supports this explanation (see Table 6, Run 18).

Storage Stability of $\text{Ce}(\text{acac})_3 \cdot \text{H}_2\text{O}$

Preference is given to the hydrous product precipitated at a pH of 8.0 by metathesis between 4.4/1.0 molar ratios of acetylacetonone and cerous nitrate hexahydrate in ammoniacal solution. Oxygen should be excluded from the stored

product to prevent its gradual oxidation to the ceric state. The storage life is lengthened to several months if the compound is sealed under vacuum or under an atmosphere of nitrogen.

Particle Size of Inhibiting Entity

A properly stabilized silicone shows little tendency to deposit inhibitor or to lose stability during one year of storage. Furthermore, the stabilized silicones can be filtered through a 0.1 micron Millipore filter with only minor losses in stabilization. A 0.1 micron upper limit for particle size is also supported by light scattering observations.

If $Ce(acac)_3 \cdot H_2O$ is stored in dry air before use in the inhibitory process, the particle size of the inhibitor increases as the storage time increases. The product stored for 8 months in dry air leads to inhibitors having maximum particle sizes ranging from 0.3 to 0.8 microns. In such a case the stabilized fluid scatters light strongly. Stabilization is still good with such larger aggregates, but 20% to 30% less efficient in the 400°C thin-film test than is the stabilization with the smaller aggregates. Filtration of the 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 to other types of silicones, using only the proportions of initial reactants known to optimize the stabilization of DC 510 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. These results are given in Tables 7-9 and Figs. 2-4.

Increased times to gelation in the 300°C thin-film tests (Table 7) indicate improvement factors ranging from 475 to 70 with several important classes of stabilized silicones. The degree of improvement decreases in the order: dimethyl silicones, lightly phenylated dimethyl silicones, lightly phenylated dichlorophenyl-substituted dimethyl silicones, moderately phenylated dimethyl silicones and tetrachlorophenyl-substituted dimethyl silicones. The lowest improvement factors are observed with the more highly phenylated dimethyl silicones such as DC 550 and DC

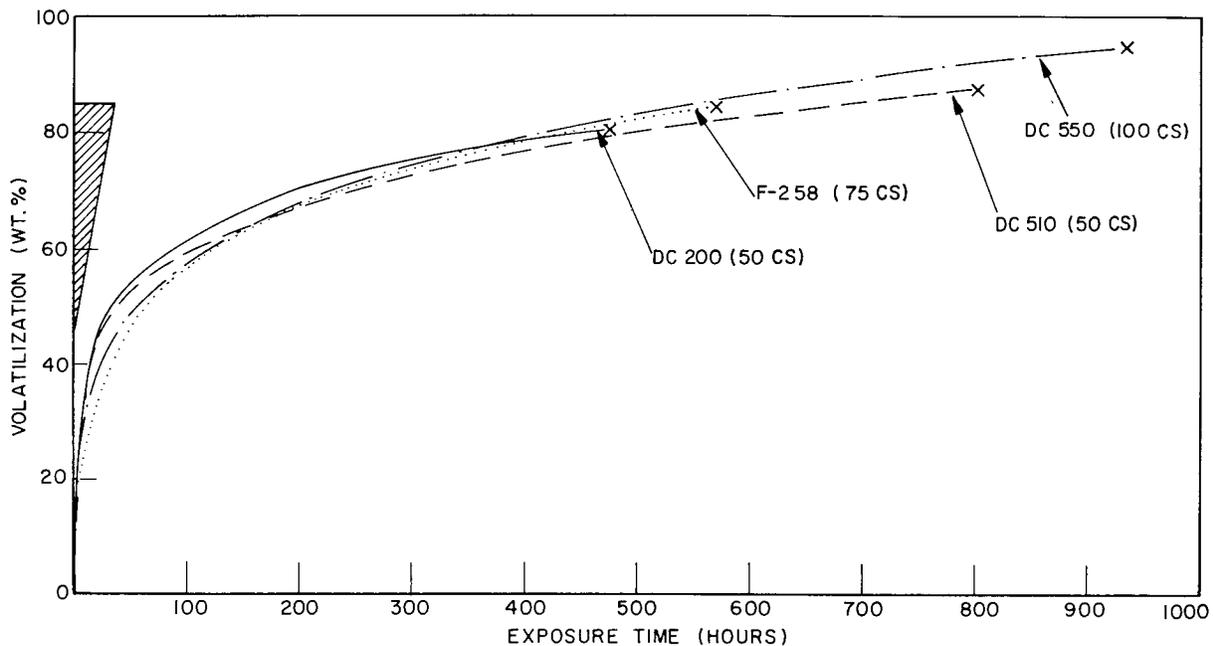


Fig. 2 — Volatilization loss vs exposure time for typical inhibited silicones in thin-film tests at 300°C. Gelation is denoted by X. Shaded wedge indicates gelation range for controls.

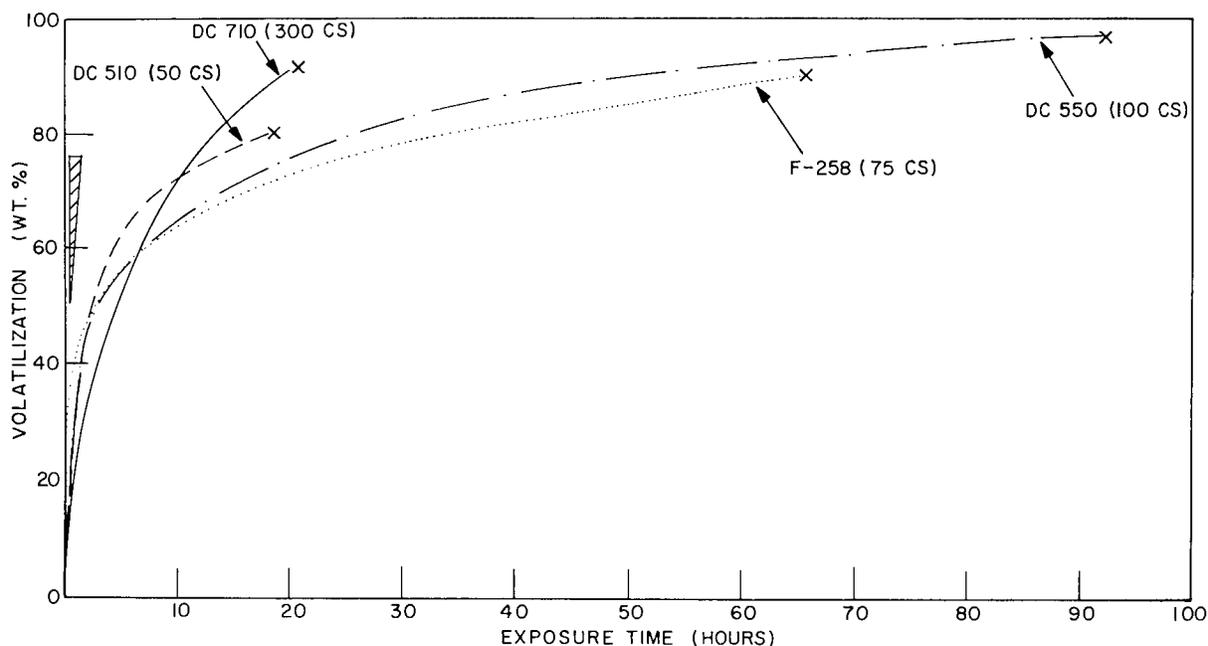


Fig. 3 — Volatilization loss vs exposure time for typical inhibited silicones in thin-film tests at 400°C. Gelation is denoted by X. Shaded wedge indicates gelation range for controls.

TABLE 7
Response of Various Silicones to Stabilization* at 300°C

| Silicone | Thin-Film Test (hr to gelation) | | Improvement Factor | Stagnation Test (hr to gelation) | | Improvement Factor |
|--------------------|---------------------------------|---------|--------------------|----------------------------------|---------|--------------------|
| | Inhibited | Control | | Inhibited | Control | |
| DC 200 (50 cs) | 475 | 1 | 475 | 162 | 65 | 2.5 |
| DC 510 (50 cs) | 800 | 2 | 400 | 245 | 135 | 1.8 |
| DC 510 (100 cs) | 700 | 2 | 350 | 200 | 135 | 1.5 |
| XF-258 (75 cs) | 1056 | 7 | 151 | 288 | 216 | 1.3 |
| XF-258 Pot Residue | 738 | 6 | 123 | 220 | 185 | 1.2 |
| F-258 (75 cs) | 570 | 7 | 81 | 242 | 216 | 1.1 |
| SF-1017 (100 cs) | 1020 | 14 | 73 | 314 | 314 | 1.0 |
| DC 550 (100 cs) | 932 | 30 | 31 | 522 | 458 | 1.1 |
| DC 710 (300 cs) | 258 | 44 | 5.9 | 550 | 440 | 1.3 |
| G.E. F-50 | 70 | 1 | 70 | 114 | 90 | 1.3 |
| D.C. F-60 | 390 | 1 | 390 | 208 | 165 | 1.3 |

*Stabilization is accomplished with the two-stage inhibitory process and the concentrate (C).

TABLE 8
Response of Various Silicones to Stabilization* at 400°C

| Silicone | Thin-Film Test (hr to gelation) | | Improvement Factor |
|----------------------|------------------------------------|---------|-----------------------|
| | Inhibited | Control | |
| DC 200 (50 cs) | 0.1 | 0.1 | 1 |
| DC 510 (50 cs) | 21 | 0.2 | 105 |
| DC 510 (100 cs) | 15 | 0.2 | 75 |
| DC 510 Pot Residue A | 15 | 0.2 | 75 |
| XF-258 Pot Residue | 75 | <0.5 | >150 |
| F-258 (75 cs) | 66 | <0.5 | >132 |
| SF-1017 (100 cs) | 42 | <0.5 | > 84 |
| DC 550 (100 cs) | 92 | 1.0 | 92 |
| DC 710 (300 cs) | 20 | 1.5 | 13 |
| G.E. F-50 | 2 | 0.2 | 10 |
| DC F-60 | 17 | 0.2 | 85 |

*Stabilization is accomplished with the two-stage inhibitory process and the concentrate (C).

710, but it should be noted that these were the most oxidation stable in the first place. The various stabilized silicones show greatly suppressed rates of volatilization in the 300°C thin-film test (Fig. 2). Improvement factors in the stagnation tests at 300°C (Table 7) 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, though not shown, gelation is accompanied by a volatility loss of 20 to 35 wt %. Baker and Singleterry have discussed the causes of the somewhat disappointing behavior of inhibited silicones in the stagnation test (7).

The results of thin-film tests at 400°C (Table 8) show that the susceptibility to stabilization at this temperature is restricted to dimethyl silicones containing phenyl substituents. Lightly and moderately phenylated dimethyl silicones give the largest improvement factors amounting to 105 and 150, respectively. The improvement factor for the more stable highly phenylated dimethyl silicone is only 13. The relationship between the times to gelation and the rates of volatilization are shown graphically in Fig. 3. The more volatile silicones (e.g., the heavily and lightly phenylated dimethyl silicones) show less

resistance to gelation than do the less volatile moderately phenylated silicones.

Some of the inhibited silicones that show good resistance to gelation in the 400°C thin-film test give signs of serious deterioration in the 400°C stagnation test. Observations made during the first 24 hours of the 400°C stagnation test (Table 9) provide a basis for excluding the less promising stabilized silicones from consideration at the higher temperature. These results show that all the stabilized silicones (except the GE F-50) resist gelation for 24 hours, but in the case of the DC 510 types of silicones and the DC F-60, deep-seated deterioration is indicated by the early appearance of the high-melting sublimate. The tendency to precipitate the inhibitor at 400°C is marked with both of the chlorophenyl-substituted silicones. On the basis of these data, both the lightly phenylated dimethyl silicones and their chlorophenyl analogs are considered inadequate for 24-hour stagnation periods at 400°C. The remaining moderate and heavily phenylated silicones are considered sufficiently stable for 24 to 48 hour periods at 400°C. Volatilization rates of the lightly and moderately phenylated dimethyl silicones observed in the 400°C stagnation test

TABLE 9
Relative Effectiveness of the Stabilization* at 400°C
(Based on Results from First 24 Hours of Stagnation Test)

| Silicone | Inhibited | | | Control | |
|------------------|------------------------|---|-----------------------------------|------------------------|--|
| | Resistance to Gelation | Time to Appearance of Solid Sublimate† (hr) | Tendency to Precipitate Inhibitor | Resistance to Gelation | Time to Appearance of Solid Sublimate (hr) |
| DC 510 (50 cs) | Good | 2 | slight | Good | 1 |
| DC 510 (100 cs) | Good | 6 | slight | Good | 1 |
| DC 510 Pot Res A | Good | 6 | none | Good | 2 |
| XF-258 Pot Res | Good | >24 | none | Good | 12 |
| F-258 (75 cs) | Good | 24 | none | Good | 12 |
| SF-1017 (100 cs) | Good | >24 | none | Good | >24 |
| DC 550 (100 cs) | Good | >24 | none | Good | >24 |
| DC 710 (300 cs) | Good | >24 | none | Good | >24 |
| GE F-50 | gels, <18 hr | 1 | marked | gels, 12 hr | 1/2 |
| DC F-60 | Good | 2 | marked | Good | 1 |

*Stabilization is accomplished with the two-stage inhibitory process and the concentrate (C).

†Amorphous cross-linked sublimate melting at 400°C analyzing as $(\text{MeSiO}_{1.5})_n$, with DC 510 silicones.

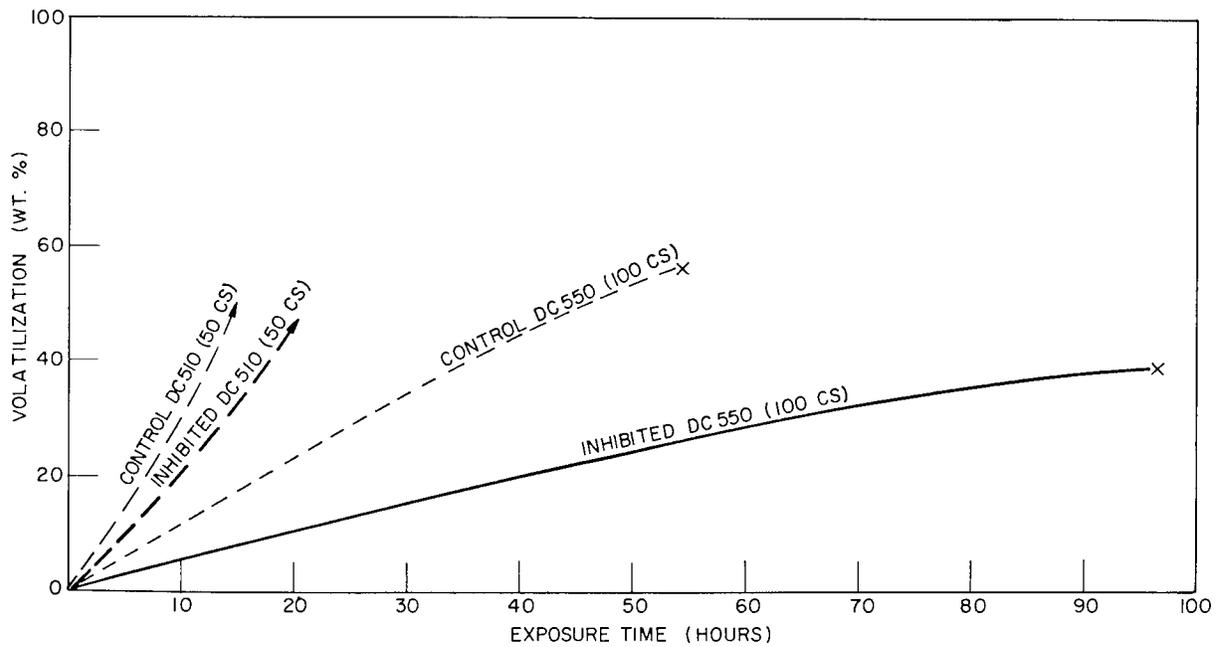


Fig. 4 — Volatilization loss vs exposure time for control and inhibited silicones in modified-stagnation test at 400°C. Gelation is denoted by X. No gelation time noted for control DC 510 and inhibited DC 510.

are shown graphically in Fig. 4. The reduced volatilization rates due to stabilization are typical and can be used to estimate the volatilization rates of related inhibited silicones.

DISCUSSION

Nature of the Inhibiting Agent

Both the physical properties and the complex nature of the MHS-Ce-silicone inhibitor make it very difficult to isolate. While explicit evidence is hard to get, a body of experimental data has accumulated which justifies some inference and speculation about the chemistry of the process by which the inhibiting entity is produced.

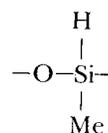
Two major postulates about the process are that (a) cerium is reacted chemically with a methylhydrogen silicone in such a way as to give a stable and catalytically active dispersion of submicronic dimensions, and (b) that the active site in the MHS is the $\equiv\text{Si-H}$ group. The inhibitor is formed in successive low-temperature and high-temperature steps which can be discussed separately.

Low-Temperature Process

The cerium acetylacetonate complex is known to react with the MHS to eliminate a minor fraction of the silane hydrogen and to give a silicone-soluble adduct in which cerium carrying acetylacetonate ligands is attached to the MHS hydrolyzate. The difficulty of reacting more than one in five of the $\equiv\text{Si-H}$ groups in the MHS with basic cerium acetylacetonates prompted the examination of steric factors involved with Stuart-Briegleb models. The two basic acetylacetonate residues shown in Fig. 5 were considered to be adducts

which satisfied the experimental observation that about one acac ligand and one $\equiv\text{Si-H}$ unit disappear during the binding of one cerium to the MHS.

Examination of model 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 $\equiv\text{Si-H}$ groups, calculations show that the ultimate H/Ce ratio is 4.5. This ratio requires that the intervening unshielded segments contain an average of 1.5



units. Experimentally, the observed H/Ce ratio is 4.2, which closely matches the 4.5 ratio estimated from the model. On this basis model A satisfies both experimental and geometrical considerations.

Measurements on model B indicate that the dimer unit can react with two hydride anions and shield another four hydride anions. If random successive additions of the dimer are assumed, together with the necessity for six adjacent unshielded $\equiv\text{Si-H}$ groups to provide reaction site for the complex, calculations show that the average unshielded segment consists of 2.5

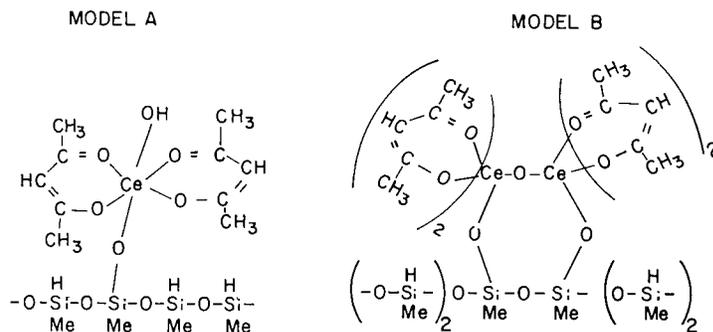
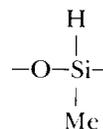


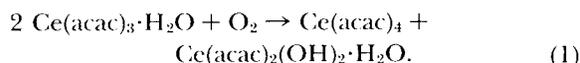
Fig. 5 — Proposed models for basic acetylacetonate residues

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. Dimer units cannot be excluded as possible attachments for the MHS hydrolyzate but it would appear that the monomer predominates in the reaction.

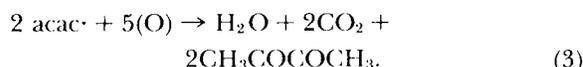
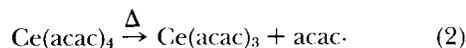
Chemistry of the Low-Temperature Reaction

The experiments on inhibition procedures have shown that a small but critical amount of water must be present to secure a highly dispersed inhibitor of optimum activity. The water present in the cerous acetylacetonate monohydrate is sufficient for the process and it has been found convenient to employ this form of cerium in the inhibiting procedure. The discussion of the reaction must then begin with the air-oxidation of the cerous ion to the ceric, before considering the reaction of the ceric compounds with MHS.

When dry air is bubbled through a solution of $\text{Ce}(\text{acac})_3 \cdot \text{H}_2\text{O}$ in benzene, the dark red color of the ceric complex appears. The resulting mixture can be resolved to yield (26) approximately one-half of the cerium as crystalline $\text{Ce}(\text{acac})_4$ and the remainder as a solution of basic ceric acetylacetonate. The main reaction can be written as:



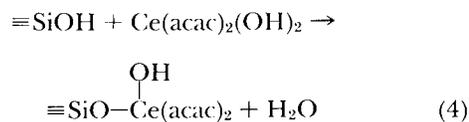
From analogy with Arnett's (26-29) study of $\text{Fe}(\text{acac})_3$, it is considered that the $\text{Ce}(\text{acac})_4$ from the above reaction may react as follows:



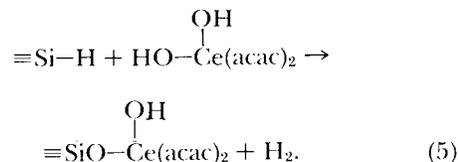
In turn the $\text{Ce}(\text{acac})_3$, with the water formed, may be expected to repeat the reaction of Eq. (1) to yield more basic acetylacetonate and water.

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

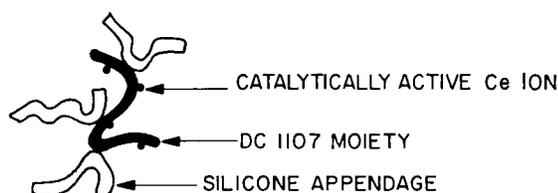


Equation (5) is supported by the fact that the number of H_2 molecules evolved closely matches the number of Ce atoms attached to the silicone.

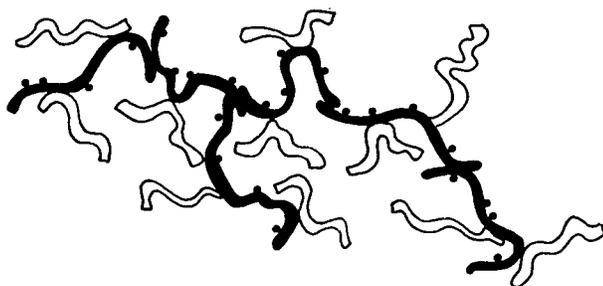
High-Temperature Process

Silicones are stabilized by aerating a mixture of the low-temperature MHS adduct with the silicone to be inhibited at 270°C. A working hypothesis permits the control and interpretation of the high-temperature process. The two essential postulates are: (a) that the silicone acts as a diluent solvent and as a reactant in the high-temperature reactions, and (b) that the required heating and aeration promote useful reactions between the MHS adduct and the silicone. The early involvement of the silicone as a reactant hinges critically on supplying the necessary activation energy. With the silicones of this study, the high-temperature generation of silanol groups can arise from the slow oxidation of methyl groups or the fast oxidation of silane hydrogens known to be present in small amount. In the case of the MHS adduct, aeration at high temperatures readily oxidizes residual silane hydrogen to silanols, and at high dilutions in the silicone solvent, these silanol groups either (a) react intermolecularly with the basic ceric acetylacetonate, (b) condense intramolecularly with themselves to form silsesquioxanes $[(\text{MeSiO}_{1.5})_n]$, or (c) 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

CONFIGURATION A: EFFICIENT SMALL PARTICLE SIZE INHIBITOR (SIZE, $< 0.1\mu$)



CONFIGURATION B: EFFICIENT LARGER SIZE INHIBITOR (SIZE, 0.1μ)



CONFIGURATION C: DETAIL OF THE SURFACE OF INEFFICIENT LARGE PARTICLE SIZE INHIBITOR (SIZE, $> 0.1\mu$)

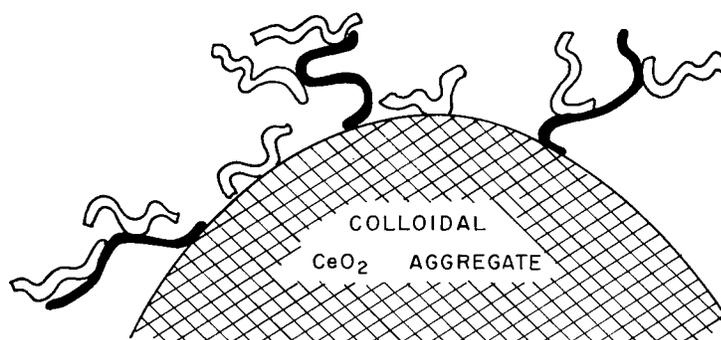


Fig. 6 - Proposed inhibitor configurations

stable macromolecule carrying cerium ions in a catalytically active form but otherwise resembling the silicone in which it is dispersed or stabilized.

Nature of the Inhibiting Entity

Evidence and arguments show that the silicone acts as a solvent and as a reactant in finishing the stabilization. These considerations, together with evidence demonstrating differences in the efficiency of inhibitors, led us to postulate three different types of inhibitor configurations, which

are shown schematically in Fig. 6 as configurations A, B, and C.

The three inhibitor configurations suggest how the efficiency of the inhibitor may vary as a function of the distribution of the catalytically active cerium ions. Inhibitor molecules ranging in structure between those in configurations A and B are believed responsible for efficient inhibition. Both filtration and light scattering experiments support this conclusion. General features of the inhibitor configurations A and B should be valid for all the silicones studied, but the number

TABLE 10
Average Molecular Weight, Density, Average Structure, Molecular Dimensions, and
Average Molecular Volume for Three Types of Silicones at 25°C

| Silicone | Average MW (g/mole) | Density (g/cm ³) | Average Structure | Mol. Dimensions* (A) | Mol. Volume† (A ³) |
|----------------|------------------------|---------------------------------|---|----------------------------|-----------------------------------|
| DC 1107 | 2560 | 0.98 | (Me ₃ SiO _{0.5}) ₂ (MeHSiO) ₄₀ | 170 × 6.7 | 4.34 × 10 ³ |
| DC 200 (50 cs) | 3500 | 0.96 | (Me ₃ SiO _{0.5}) ₂ (Me ₂ SiO) ₄₅ | 150 × 7.0 | 6.06 × 10 ³ |
| DC 510 (50 cs) | 2600 | 1.00 | (Me ₃ SiO _{0.5}) ₂ (Me ₂ SiO) ₂₇ (MeO)SiO) ₃ | 110 × 11 | 4.32 × 10 ³ |

*Observed from measurements made with Stuart-Briegleb molecular models, full extension of chain assumed.

†Calculated volume per molecule.

of silicone chains attached to the DC 1107 moiety could vary depending on the reactivity of the silicone.

Configuration C results when the basic ceric oxide residues formed during pyrolysis and oxidation of the acetylacetonate ligands condense with themselves to form an inorganic colloid particle covered with chemically linked silicone molecules. It is thought to correspond to the 10 to 0.1 μ colloids encountered in many of the early preparations from disalicylalpropylene-diamine Ce(IV) complexes and in the less satisfactory variants of the two-step process reported here. The colloid does not pass through a 0.1 μ filter; it is probable that it blocks the pores against the passage of any A or B type inhibitor molecules that may be present with it so that the clear filtrates from such hazy systems exhibit little or no better stability than the uninhibited starting silicone. The conditions for the two-step inhibitory process have been selected to minimize the formation of the large colloid particles, which may sequester a major fraction of the cerium ion in unavailable locations.

The relation of inhibitor particle size to inhibition efficiency is clarified by a consideration of the average volume of silicone liquid associated with each inhibiting unit. This volume can be computed from the data of Table 10, under the simplifying assumption that calculations based on average polymer size will apply approximately to the mixture of sizes actually present. These calculations show that 590 molecules of the 50 cs dimethyl silicone are present with each molecule of the cerium-MHS complex. These molecules

will occupy 3.57×10^6 cubic Angstroms, which would fill a cube 153A on a side. Since the fully extended length of the MHS molecule is estimated from molecular models to be 169A, it is apparent that activated points in a silicone molecule which might be subject to attack, or activated oxidizing agents, would have a good probability of encountering an active inhibitor group by thermal diffusion within a time conveniently measurable in nanoseconds. If the weight percent of inhibitor is held constant, the probability of encountering an active inhibitor group decreases as the cube root of the molecular weight of the inhibitor. Accordingly, increasing the size of inhibitor configuration A by respective factors of 8 and 1000 would be expected to lower the inhibitor efficiency by factors of 2 and 10.

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| 14. KEY WORDS | LINK A | | LINK B | | LINK C | |
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| | ROLE | WT | ROLE | WT | ROLE | WT |
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