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# **Hypothesis of Siloxane Degradation at High Temperature and the Effect of Cerium-Based Inhibitor**

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## ABSTRACT

The cerium-based inhibitor for extending gelation times of commercial silicones is considered from the standpoint of the relatively fixed proportions of reactants necessary for optimum stabilization. A connection is made between these fixed proportions and the hydride/silanol content of the commercial silicone itself. The release of  $H_2O$  by the high-temperature condensation of silanol groups does not lead to the simple evolution of  $H_2O$  vapor but rather to a rapid catalytic attack by  $H_2O$  on the siloxane chain. The beneficial effects of the cerium inhibitor can be rationalized in terms of eliminating the source of high-temperature  $H_2O$  evolution.

## PROBLEM STATUS

This is an interim report; work on this problem is continuing.

## AUTHORIZATION

NRL Problem C07-04  
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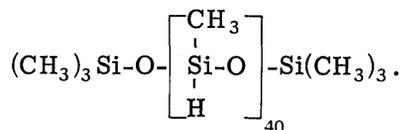
# HYPOTHESIS OF SILOXANE DEGRADATION AT HIGH TEMPERATURE AND THE EFFECT OF CERIUM-BASED INHIBITOR

## INTRODUCTION

The polysiloxanes of the general formula  $(\text{CH}_3)_3\text{Si}(\text{RR}'\text{SiO})_x\text{Si}(\text{CH}_3)_3$ , where R is a methyl group and R' is a methyl or phenyl group, possess thermal and oxidative stabilities which make them useful hydraulic fluids up to temperatures of about 250°C. Trace impurities, particularly metals, are known to catalyze the degradation of polysiloxanes (1). Anaerobic pyrolytic breakdown becomes significant above 300°C (2).

Various additives have been developed which extend the useful high-temperature limit of the polysiloxanes to 300°C and beyond (3). Of the many procedures used to stabilize silicone fluids, perhaps the most successful has been the cerium acetylacetonate process developed at NRL in 1965 (1,3,4). The presence of only 0.025 wt-% cerium extended gelation times far beyond those obtainable with other inhibitors—useful life at 400°C was equal to that previously achieved at 300°C.

This report describes further work on one of the most interesting features of the cerium process—the relatively fixed proportions required for optimum stabilization. Briefly, the stabilization process is accomplished in two separate steps, the first of which involves the reaction between cerous acetylacetonate monohydrate (or ceric acetylacetonate plus  $\text{H}_2\text{O}$ ) and a long chain silicone hydride (DC 1107), whose average structure is



The fixed proportions were 3.69 moles  $\text{Ce}(\text{acac})_3 \cdot \text{H}_2\text{O}$  to 1.00 mole DC 1107 reacted in refluxing benzene with dry aeration. After a reaction time of 1 hour, infrared measurements indicated that three of the 40 hydride groups in DC 1107 were lost, being presumably replaced by some other substituent group. The product(s) of this reaction is referred to as adduct I and is assumed to be a simple derivative of DC 1107 in which three hydride groups have been replaced by a new substituent moiety whose exact nature remains to be established.

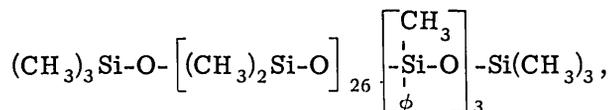
In the remainder of this report, the term "trisubstituted" is used with reference to these modified DC 1107 (adduct I) molecules. This entire reaction mixture is used in the second step, which involves dilution with sufficient silicone fluid to attain a final concentration of cerium (all forms) equal to 0.025% after the benzene is removed. Either decreasing or increasing the 3.69:1.00 proportion in the first step, or the 0.025% figure in the second step, causes a major decrease in gelation times from their maximum values. The highly specific effect of these fixed proportions strongly implies a specific degradation pathway in the polysiloxane molecule, involving species which, although present in low concentration, are of potent significance in determining the rapidity of the overall gelation reaction.

## MATERIALS AND PROCEDURES

The particular silicone used as a representative fluid was Dow-Corning DC 510 (100 cs), a lightly phenylated dimethyl polysiloxane possessing the properties

$$\begin{aligned}\phi/\text{CH}_3 &= 0.05 \text{ (molar ratios),} \\ \text{average mol wt} &= 2,600, \\ \text{density} &= 1.00 \text{ g/ml, and} \\ n_D^{20} &= 1.4256.\end{aligned}$$

If it is assumed that the phenyl groups are singly substituted to silicon in the chain, the average structure may be represented as



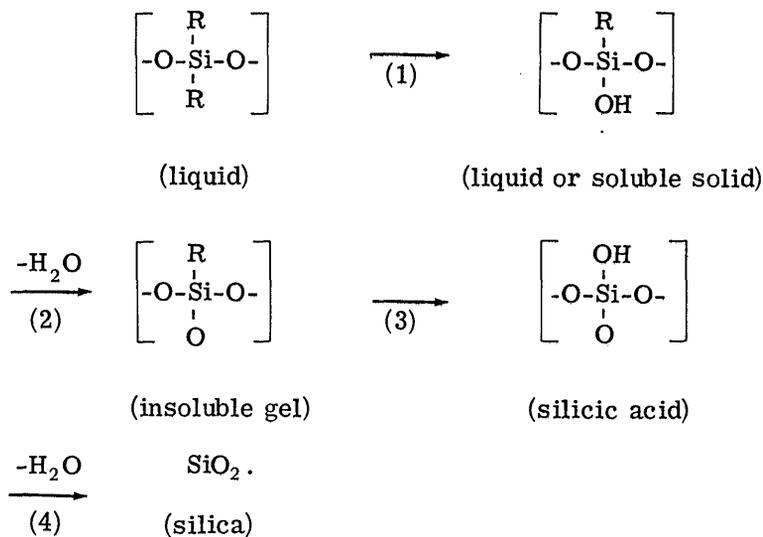
in which three (at random) of the 29  $-\text{R}_2\text{SiO}-$  groups in the chain contain one phenyl substituent. For most commercial silicone fluids, a considerable range of structures and molecular weights is included in such averages. All other chemicals used were commercially available C.P. or reagent-grade materials.

Gelation tests involved a minor variation of the heated-plate test (4) and were always conducted at 400°C. Ordinary cover glasses, 22 mm in diameter and 0.2 mm thick, were used to support 1 ml of the test silicone. Blanks were always run, using untreated DC 510. For several hundred blanks, the time required for gelation was 6 to 12 minutes with the majority of samples being 6 to 8 minutes. This agrees with the figure of 0.1 hour (6 minutes) obtained previously (4). Consequently, 0.1 hour is defined as the normal gel time for this silicone fluid. The empirical improvement factor (IF) is the ratio of test gel time to normal gel time. Thus, a procedure which extends the time required for gelation to 2 hours has an IF of 20. The cerium procedure had given an optimum gel time of 4.2 hours and a corresponding IF of 42. These quantities should be kept in mind in the ensuing discussion. If indeed there is some specific gelation pathway associated with the silicone itself, then such figures represent control over that pathway due to the cerium process. Any substance capable of exerting similar control should produce comparable (though not necessarily identical) improvement. Comparison between active substances of dissimilar structure may disclose only one or two common features and thereby delimit the nature of this pathway.

## INITIAL APPROACHES

## Role of Silanol Condensations

Within the general problem of thermo-oxidative degradation of silicones, the principal uncertainty concerns the initial or primary reactions. The silicone liquid is partially converted to gaseous cyclics and linear structures, corresponding to decreases in molecular weight; the remainder of the liquid forms a gelatinous solid (gel). The ultimate product in the condensed phase is the predictable  $\text{SiO}_2$ , regardless of original structure or intermediate mechanism. Silica is formed by the silanol formation-condensation sequence



What remains to be established is exactly how the lower-molecular-weight volatiles are formed and exactly how reactions 1 and 3 take place. On the other hand, the role of inorganic silanols as precursors of  $\text{SiO}_2$  (reaction 4) and organic silanols as precursors of gels (reaction 2) is well established.

In view of reactions 2 and 4, it seemed remarkable that a relatively rich source of silanol groups (adduct I oxidized in the high-temperature step) could be used to stabilize silicones by delaying the gelation process.

To investigate this interesting role of silanols, additional consideration was given to the proportions of the low-temperature step, as detailed in Ref. 4. The most effective number of substituents was three, and a maximum of eight positions could be substituted in DC 1107. This indicates that each substituent blocks a total of five positions - one by direct bonding and two on either side by steric hindrance. According to this model, substituents must be separated by at least five chain units and be at least two chain units away from the terminal end groups. Random substitution along the chain within these assumed conditions would yield position isomers. It is noteworthy that the number of position isomers increases from 18 for one substituent and 256 for two substituents to a maximum at three and four substituents, then decreases beyond four substituents back to the single isomer with eight substituents.

Now the number of substituents and the resulting number of position isomers should exert considerable effect over subsequent condensations of the remaining silanol groups (from air oxidation of hydride groups). First, the size and number of substituents influences the rate of condensation. The temperature required for appreciable condensation of trisubstituted DC 1107 (adduct I) is considerably higher than that of DC 1107 itself, which rapidly condenses and gels at  $180^\circ$  to  $200^\circ\text{C}$ .

A second point concerns the extent of crosslinking between silanol groups in oxidized adduct I species and oxidized DC 510 species. In this connection, it is of interest to calculate an approximate range of silanol concentration due to oxidized adduct I in the stabilized fluid, based on the original proportions of DC 1107,  $\text{Ce}(\text{acac})_3 \cdot \text{H}_2\text{O}$ , and DC 510. This simple calculation gives a concentration of DC 1107 =  $5.0 \times 10^{-4}\text{M}$  in DC 510 solution after the benzene is removed. If all the DC 1107 is assumed to be in the trisubstituted form of adduct I, there remain 37 hydride groups which may oxidize to silanol. The

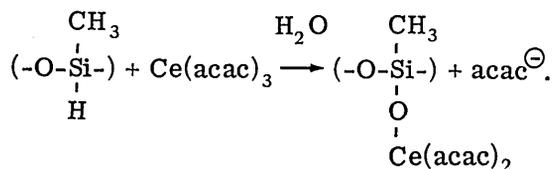
silanol concentration due to oxidized adduct I might then be as much as  $1.9 \times 10^{-2}$  M for a calculated upper limit. The approximate silanol concentration range from oxidized adduct I is then considered to be  $10^{-3}$  to  $10^{-2}$  M.

#### Role of Acetylacetonate

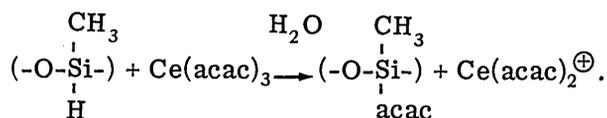
One of the strongest traditions in the development of silicone additives has been to use organometallic compounds, such as transition metal soaps (4). The cerium process was itself an improvement of an earlier procedure involving a cerium-disalicylalpropylenediamine chelate (5). As the authors point out (4), the cerium acetylacetonate-DC 1107 process increased the stabilization temperature (as measured by gel times) to  $400^\circ\text{C}$  from  $325^\circ\text{C}$  for the older, cerium-diamine chelate process. Since the rate of the gelation reaction drastically increases with temperature above  $325^\circ\text{C}$ , a  $75^\circ$  extension in reproducible stabilization is a rather large "jump."

Since both stabilization processes involved cerium, it is certainly reasonable to assume that in each case cerium is the active inhibitor. Also, many of the samples from the older cerium procedure were as well stabilized as those from the newer procedure. This may simply indicate that the procedure involving adduct I achieved a more effective dispersion of the cerium due, for example, to more uniform particle size or to solubilization of the additive.

With full acknowledgment of the experimental observations which implicate cerium in the inhibitory mechanism, it nonetheless arouses suspicion that undeniable improvement is brought about by the inclusion of one of the very few chemical species toward which silicon readily exhibits pentacovalency and hexacovalency - the acetylacetonate ion (6). The infrared analysis of the reaction leading to adduct I showed that one  $\equiv\text{Si-H}$  unit was consumed for each  $\text{acac}^-$  lost from  $\text{Ce}(\text{acac})_3$  (4). Based on these facts, the reaction could be written as



The same facts equally support another alternative, however;



Experiments were therefore conducted to ascertain any independent role of acetylacetonate. Water was not included in this initial approach, because it was presumed to be simply an ionizing solvent for  $\text{Ce}(\text{acac})_3$  and therefore dispensable if ionization could be otherwise accomplished.

The addition of 5 to 10 vol-% of acetylacetone to DC 510 fluid, followed by heating for 30 minutes at  $100^\circ\text{C}$ , gave a solution having a reproducible IF of 2. Ionic acetylacetonates (ammonium, barium, sodium, and potassium acetylacetonates) were of no effect, being insoluble in DC 510 and undergoing separate (and expected) decompositions on heating.

Better results were obtained if DC 1107 was used in a preliminary step before combining with DC 510. Two acetone solutions, one containing 10 vol-% of acetylacetone and the other saturated with sodium acetylacetonate, were treated with 1 ml of DC 1107 each, then combined with 20 to 30 ml of DC 510 to obtain 3- to 5-vol-% solutions. The acetone was evaporated, and the conditions of the high-temperature step (4) were employed for processing. The reproducible IF was 4 in each case, still far away from the cerium IF of 42 but twice as good as acetylacetone itself.

The IF of 4 was too large to be ignored but too small to offer much encouragement. There was no question about a reaction occurring between DC 1107 and the acetylacetonate species nor about the beneficial effect of the product. However, if the most important inhibiting species was a DC 1107-acetylacetonate adduct rather than a DC 1107-cerium adduct, it was concluded that some important reaction species present in the cerium procedure had been omitted in these experiments.

### Role of Water

One of the well-known properties of silicones is their immiscibility with  $H_2O$  and the use of silicon hydrides as waterproofing agents. It is not so well known that a strong physical interaction occurs through slow orientation of polysiloxane films on  $H_2O$  surfaces (7) and that the Si-O-Si bond may be broken with  $H_2O$  at elevated temperatures (Ref. 2, page 222; Ref. 7, page 731; and Ref. 8).

The condensation of silanol groups produces  $H_2O$  as well as crosslinks (reactions 2 and 4). As the condensation temperature increases above  $100^\circ C$ , both the rate of simple evaporation and the rate of active attack will increase. The fact that one is studying a condensation-gelation reaction at a temperature several hundred degrees above the boiling point of  $H_2O$  does not necessarily mean that the  $H_2O$  generated in the reaction plays an inert role.

Another reason for becoming interested in a possible specific role for  $H_2O$  comes from the cerium process, in which  $H_2O$  must be present in fixed proportions in the low-temperature step.

Several different types of experiments were performed to explore this possibility. Most of the results provided no new information but simply agreed with previously established facts: commercial silicone fluids contain trace amounts of  $H_2O$  which is evolved at  $100^\circ C$ ; somewhat larger amounts of  $H_2O$  are generated during thermal oxidative degradation and gelation.

The evolution of small amounts of  $H_2O$  from DC 510 at  $400^\circ C$  may be observed by the color change of indicating Drierite or the swelling of BaO. If either solid is placed directly in the silicone, no  $H_2O$  is indicated until gelation occurs, at which point sudden liberation of  $H_2O$  is observed.

Indicating Drierite (anhydrous  $CaSO_4$  desiccant) caused no effect on gel times, whereas BaO altered gel times in a very erratic fashion, ranging from harmful effects (IF = 1/3) to very beneficial effects (IF = 18). This latter figure indicated that the removal of  $H_2O$  by drying agents was not necessarily detrimental but might even extend gelation times.

Water may be observed also by distillation of volatiles from DC 510 at  $400^\circ C$ . The cumulative yield of  $H_2O$  vapor, including that which is liberated on gelation, was in the range 0.5 to 1.0 wt-%. This is much higher than that obtained when oxygen is absent or when the amount from gelation is not included.

A somewhat different approach was more informative. In cerium-inhibited silicones, the principal source of  $H_2O$  is presumably from oxidation and condensation of adduct I. If  $H_2O$  is actually a reactant as well as a product in the overall gelation process, its effect will not be seen until crosslinking begins, since it is not otherwise present at elevated temperatures. Experiments with diphenyl silanediol -  $\phi_2Si(OH)_2$  - indicated that this might be the case. Diphenyl silanediol is very highly hindered and requires several hours for intermolecular condensation, even at elevated temperatures (9). Solutions in DC 510 were prepared, ranging from extremely dilute (ca. 0.01%) to saturated (ca. 10%). There was no effect whatsoever on gel times, which were identical with blanks. Silanols must condense to form the crosslinks of gels, of course; they must also condense to generate  $H_2O$ , but there is apparently no other important gelation effect of silanols per se.

At the other extreme of silanol reactivity is the oxidized or hydrolyzed derivative of DC 1107 itself. In the range 1 to 10 wt-% of DC 510, considerable gelation occurs rapidly on either direct heating to 185° to 200°C or warming to 40°C in acetone containing a few percent  $H_2O$ . A small quantity of gel may be isolated by filtration from the acetone solution at the level of DC 1107 used in the cerium process (0.13%).

If gels obtained from DC 1107 are digested in DC 510 solution at 100° to 120°C for 1 hour, they may be filtered from the silicone fluid in an apparently quantitative yield, with the clear filtrate possessing a normal gel time.

These results from DC 1107 indicated that even vigorous silanol condensations, producing both crosslinks and  $H_2O$ , do not appreciably affect the DC 510 silicone itself below 200°C.

The temperature range of silanol condensation- $H_2O$  generation which now remained unexplored was 200° to 400°C. To bridge this region, inorganic silicates of Group IA were employed, with remarkable results. Sodium metasilicate ( $Na_2SiO_3 \cdot 9H_2O$ ) loses six  $H_2O$  molecules at 100°C to form the hypothetical  $Na_2Si(OH)_6$  structure. Whatever may be the exact structure of this compound, it is a silanol which condenses with the liberation of  $H_2O$ , a process beginning at 100°C and continuing up to 1088°C - the melting point of anhydrous  $Na_2SiO_3$ . This material was insoluble in DC 510, and on heating to 100°C, the crystals dehydrated as expected. No further reaction occurred until the temperature reached 300°C, at which point a very vigorous reaction ensued, quickly converting over 90 vol-% of DC 510 to gaseous products. Further, this was a catalytic effect: 1 mg of  $Na_2SiO_3$  converted 30 ml of DC 510 to gaseous products, leaving behind only a small surface residue.

Potassium and lithium silicate were not as potent as  $Na_2SiO_3$  but gave the same type of effect only if the temperature was at least 300°C.

Since the temperature of 300°C does not correspond to any sharp transition point of sudden dehydration for these three inorganic silicates, this transition effect toward  $H_2O$  attack appears to be due to the siloxane itself. Whether such a conclusion is justified<sup>2</sup> remains to be seen. However, it is noteworthy that there is reported evidence for a helical structure of linear polysiloxanes and for a presumed helix-random coil transition at elevated temperatures (2).

#### Selected Chemical Analyses of DC 510

The complex interrelationships among silicone hydrides, silanols,  $H_2O$ , crosslinkage, etc., have some parallel in the history of commercial silicone manufacturing. The very first batches of silicone fluid submitted for testing were so rich in hydride content that rapid gelation occurred below 200°C (10). As commercial synthesis was gradually improved, hydride content was reduced and gelation temperatures increased.

Presently, the hydride content of silicone fluids is low and variable, ranging from no detectable content up to as much as  $10^{-2}$  M. Even at the upper end of this range, the level is just beyond the present sensitivity of proton-NMR for siloxane hydrides and detectable only with great difficulty by the more sensitive IR spectroscopy (1) technique. One way to overcome the analytical problem of low relative content is to chemically treat a large volume of silicone fluid with alcoholic KOH and measure the volume of  $H_2$  liberated. One such analysis of DC 510 gave a hydride concentration of  $4 \times 10^{-3}$  M (11), although experimental errors require that this simply be treated as an order of magnitude or range ( $10^{-3}$  -  $10^{-2}$  M).

Apart from hydride content, present silicone fluids seem remarkably free of foreign impurities. Specific analyses for four common metals and three common nonmetallic elements were obtained during this study, and the results are given in Table 1.

Table 1  
Specific Element Analysis of  
DC 510 Silicone

Element	Amount (ppm)	Method
Al	1	Spectrochemical
Cu	1	Spectrochemical
Mg	1	Spectrochemical
Fe	(not detected)	Spectrochemical
P	0.1	Neutron activation
S	0.4	Neutron activation
Cl	7	Neutron activation

The last two elements are of significance in that chlorosilanes are starting materials for the preparation of many commercial silicones, and sulfuric acid is a common polymerization catalyst. The impurity present in greatest amount was chlorine, the 7 ppm of which correspond to a  $\equiv Si-Cl$  concentration of  $2 \times 10^{-4}$  M.

On the basis of the impurities considered, the only significant impurity appeared to be residual hydride.

#### HYPOTHESIS OF SILOXANE DEGRADATION AT HIGH TEMPERATURE AND THE EFFECT OF CERIUM-BASED INHIBITOR

To begin with, this is an hypothesis, not a theory. Arguments are presented as specifically as possible in order to be open to direct attack rather than because of any confidence concerning their absolute accuracy.

It is considered that all silicone fluids of the general type under investigation acquire a hydride content of  $10^{-3}$  to  $10^{-2}$  M during initial synthesis. Depending on the processing, separation, purification, and storage conditions, some or all of the hydride may be oxidized or hydrolyzed to silanol. Absence of hydride content then means that quantitative conversion to silanol has taken place; it does not reflect any absolute purity of the

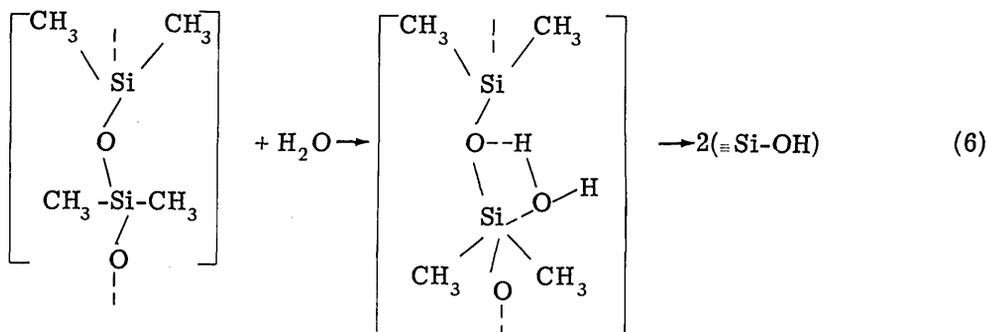
silicone itself. A range of hydride content is obtained from various samples depending on their individual histories; but the total impurity (hydride plus silanol) remains fixed in the range  $10^{-3}$ - $10^{-2}$  M.

As the silicone is heated above  $300^{\circ}\text{C}$  in air, any remaining hydride groups are oxidized to silanol. Due to the low concentration of silanol groups and high steric hindrance, the initiation of condensation requires several minutes even at  $400^{\circ}\text{C}$ . Once started, however, the reaction is enormously accelerated by the catalytic attack of  $\text{H}_2\text{O}$ , postulated to take place as follows:

#### Initial Condensation



#### Attack of $\text{H}_2\text{O}$ on Siloxane Chain



#### Secondary Condensation and Regeneration of $\text{H}_2\text{O}$



Reaction 5 lengthens the chain and leads directly to gelation; reaction 6 shortens the chain by producing two separate silanol structures; reaction 7 leads to cyclics if intramolecular and to either linear structures or gels in intermolecular. Secondary silanols produced in reaction 6 are terminal groups in contrast to the initial silanols arising from original hydride, which are probably chain groups. There are then both terminal and chain silanols available for condensation, a combination which, like the monofunctional and difunctional combination used in siloxane synthesis, permits a variety of structures to be obtained.

The postulated pentavalent silicon intermediate may cleave as shown with an energy requirement essentially that of the ionization of  $\text{H}_2\text{O}$ . The silicon-oxygen bond is transferred between two oxygen atoms, rather than being literally "cracked." The postulated intermediate could also be simply comprised of the  $\equiv\text{Si}\cdots\text{OH}_2$  species, without the additional hydrogen bond to a chain oxygen. In this latter case, the silicon-carbon bond is open to attack, producing methanol and its oxidized derivatives and leaving behind a silicon hydride. This oxidizes to more chain silanol and on condensation restores the level of  $\text{H}_2\text{O}$ .

The  $\text{H}_2\text{O}$  itself is continually recycled (7), becoming immediately bound in another complex (6), and surrendered by the silicone only on final gelation.

The cerium inhibitor is then considered to delay gelation by forcing condensation of available silanol groups in the siloxane to occur below the temperature of catalytic H<sub>2</sub>O attack. After the reaction mixture from the low-temperature step is combined with silicone fluid and benzene is removed, the processing temperature is maintained at 285°C, which is sufficiently below the temperature of H<sub>2</sub>O attack to allow complete removal of H<sub>2</sub>O as vapor. Available silanols from adduct I must match the level of silicone silanols; too much or too little will leave behind excess silanols which will condense and generate H<sub>2</sub>O at the higher temperature of 400°C.

This abortive condensation eliminates all high-temperature sources of H<sub>2</sub>O, thereby removing a species which causes degradation within minutes and leaving only the purely thermooxidative decompositions which are slow at 400°C.

Finally, it should be stressed that this hypothesis constitutes an addition to, rather than a detraction from, the many theories of siloxane degradation. Catalytic H<sub>2</sub>O attack at 400°C is considered to be the fastest route to gelation; it is by no means considered to be the only route.

#### FUTURE WORK

Further attempts will be made to form a silicon-acetylacetonate linkage from a silicon-hydride linkage. In addition to serving as a check on the cerium hypothesis, such compounds might allow the extension of the silicon-acetylacetonate combination to polysiloxane polymers. All of the reported combinations appear to be low-molecular-weight compounds: the well-known tris-acetylacetonate of silicon itself, bis-acetylacetonates of silicon esters (12) and organosilicon halides (13), and mono-acetylacetonates of certain organosilicon halides (13).

Other approaches would involve removing or reacting residual hydride-silanol impurities present in commercial silicones to ascertain if this caused major improvement in thermal stability. The discovery of the significance of hydride content made by previous authors (1,3,4) continues to be the most promising line of attack.

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14. KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
Siloxane degradation Cerium-based inhibitor Silicones						