High Temperature Antioxidants for Hydraulic Fluids and Lubricants

Evaluation and Mechanism of Protection of a Silicone Fluid

EDWARD M. ACTON, KATHLEEN E. MORAN, and ROBERT M. SILVERSTEIN
Stanford Research Institute, Menlo Park, Calif.

EFFICIENT antioxidants are needed to protect the hydraulic fluids and lubricants used in modern aircraft from oxidative degradation at high temperatures. The compounds evaluated as high temperature antioxidants (Table I) fall into two main classes: (1) aromatic and heterocyclic compounds, and (2) organometallic compounds.

EVALUATION

SCREENING PROCEDURE AND APPARATUS

Air, or a mixture of 95% nitrogen and 5% oxygen, was bubbled at 1 liter per hour through lubricating fluid (20 grams) containing the dissolved additive under test, and several polished metal washers (immersed, spaced on the inlet tube). Table II presents the fluids used, and temperature, duration of test, type of gas, and combination of metal washers for each fluid.

The principal criterion for effectiveness as an antioxidant was the ability to retard viscosity increase. This was determined by comparing the fluid containing additive with the fluid containing no additive. Kinematic viscosities were determined at 100° and 210° F. Other effects measured were net weight change of fluid, acid number, petroleum ether-insolubles, and weight change of metal washers. Oxygen consumption was tested on a number of runs. Some of the oxidative degradation products were identified and measured by analyzing infrared spectra, vapor phase chromatography, and mass spectrographic data.

A Wright Air Development Center (WADC) design (10) for a high temperature bath was followed with slight modifications. The design of a micro-oxidation–corrosion test tube (11) was modified to permit sampling of the exhaust gases. The inlet tube tip was $\frac{1}{16}$-inch inside diameter and was centered $\frac{1}{4}$ inch from the bottom of the test tube. Twenty grams of fluid were used in each tube for screening.

Dry cylinder gas flowed through a pressure regulator, a needle valve, a mercury manometer, and a precautionary drying tube to a manifold, to which were connected, in parallel, six (or eight) flowmeters (Tri-Flat Flowmeter, tube 08F-1/16-08-4, float SA-16 sapphire, 0–40 cc. per minute, Fischer and Porter Co.). At the top of each flowmeter was a metering valve (Hoke No. 4 RB 281) connected with Tygon tubing and a 12/5-ball joint to the inlet of the adapter on the micro-oxidation–corrosion test tube. Gas thus bubbled through the test fluid, up through the reflux condenser, through a three-way stopcock on the exhaust manifold (the stopcock permits either sampling or venting). The exhaust manifold was a horizontal glass tube 17 inches long and 1½ inches in diameter, sealed at both ends and fitted with three-way stopcocks, a drain, and a vent.

Metal washers were cut from 0.032-inch sheet of the folowing specifications.

Aluminum, Federal specifications QQ-A-3-55, temper T_3 or T_4
Titanium-Mil-T-7993A
Steel-1005, Federal specifications QQ-5-636, cold-rolled
Silver-Electrode
Copper-QQ-6-501

Washers were cut, polished, and handled in accordance with WADC specifications (12).

DISCUSSION

F-50 Silicone Fluid. This fluid (General Electric, Versilube) is a dimethylsilicone polymer in which one out of 55 methyl groups is replaced by a 2,3,5,6-tetrachlorophenyl group. The end groups on the chains are trimethylsiloxy groups. The average molecular weight is 3000, corresponding to an average chain length of about 40 units (6).

F-50 silicone fluid has a fairly low oxygen tolerance at elevated temperatures. When dry air was bubbled through a 20-gram sample of the unprotected fluid at 1 liter per hour at 518° F., it gelled in an average time of 10.4 hours; the presence or absence of washers had no discernible effect on gel time. At 550° F. with a mixture of 5% O_2–95% N_2, gel time with washers was 27.8 hours (4 runs); without washers it was 23.0 hours (4 runs). More runs are necessary to establish the validity of this apparent effect of washers at 550° F. Oxygen consumption measurements with a Beckman oxygen meter showed that 18.2% of the oxygen supplied at 518° F. over a 10-hour period was consumed. This represents 7.5 $\times$ 10^{-5} mole of O_2 per gram of fluid per hour, or 0.24 mole of O_2 per mole of fluid per hour based on a 20-gram sample of molecular weight 3000.

Most of the additives in F-50 silicone fluid were screened at a concentration of 0.2% at 518° F., with dry air for 48 hours. The unprotected fluid, of course, was gelled at the end of the 48-hour period. Many additives were able to prevent gelation for this period, including several that were effective in preserving the integrity of the test fluid. Condensed aromatic ring compounds containing three or more rings were effective as a class. Anthracene, with its three linearly fused rings, sets the lower limit of activity; phenanthrene, with its three angularly fused rings, is much more effective. Naphthalene is not active, but 1,1-binaphthyl is. Acenaphthene, which is simply naphthalene with an ethylene bridge, shows high activity. However, attempts to correlate structure with activity must take the influence of volatility into consideration. More compounds should be tested before attempting to correlate activity with number of rings and configuration. In addition to the coherent groups of compounds, there were several other effective additives of diverse structure: dinaphthalenethiophene; 2,5-diphenyloxazole; mixed thujaplicins (slight effectiveness); N-phenylferrocenecarboxamide; 4,4'-bis(dimethylamino)benzophenone; and Indanthrene Navy Blue BRA powder.

At 550° F. with a mixture of 5% O_2–95% N_2, the unprotected silicone fluid was gelled within 48 hours, and the gel was discolored (at 518° F. the gel was clear yellow). Some of the additives were still effective at 550° F., though less so than at 518° F. in spite of the fact that gel time of the untreated fluid was longer at the higher temperature.

At 700° F. with a mixture of 5% O_2–95% N_2, the unprotected silicone fluid was gelled at the end of a 10-hour period, as was the fluid containing additives effective at the lower temperatures. The test period was therefore reduced to 5 hours; at the end of this time, the unprotected fluid

was opaque and dark brown, but only moderately viscous. The average viscosity increase (100° F.) for the unprotected fluid was 114% (4 runs) but the fluid containing additives was gelled at the end of 5 hours. These observations set an upper temperature limit at which the additives cease to be effective. Fluid weight losses would have been high without condensers, because active refluxing occurred. Pyrolysis probably complicates the picture at this temperature.

The criteria used to establish an order of general effectiveness for the additives under test were ability to retard viscosity increase, low-temperature solubility, appearance of fluid (darkening or sludging), and toxicity considerations. Gross weight change, acid number, and washer weight changes were not consistent criteria. The effective antioxidants caused neither unusually high acid numbers, nor excessive attack on the washers.

Effectiveness in retarding viscosity increase was evalu-

Table I. Compounds Evaluated as Potential Antioxidants[a]

Aromatic and Heterocyclic Compounds

2,2'-Dipyridylamine (RTC)
1,2-Benzanthracene (A)
2-Benzylbenzimidazole (A)
1,1'-Binaphthyl (A)
9-Bromoanthracene (A)
8-Bromotheophylline (A)
2-Chloro-5-methylnitrobenzene (A)
Cholesterol (A) (fused rings but not aromatic)
9-Cyanophenanthrene (A)
Decacyclene (A)
Difluorenyl (A)
Dinaphthylenethiophene (A)
1,3-Dinitro-2,4,5-trichlorobenzene (A)

Di-p-tolylsulfoxide (A)
2,6-Lutidine-N-oxide (A)
4-Bromobiphenyl (EK)
2-Methoxydiphenyl ether (A)
6-Methoxy-8-nitroquinoline (A)
2-Methyl-3-p-nitrophenylquinoxaline (A)
1,10-Phenanthroline (A)
m-Terphenyl (A)
Chrysene (EK)
7,8-Benzoflavone (EK)
Brucine sulfate (EK)
Caffeine (EK)
6-Dimethylaminoquinaldine (EK)
4-Iodobiphenyl (EK)

2-Methyl-1-nitroanthraquinone (EK)
4,4'-Bis(dimethylamino)-benzophenone (EK)
4,4'-Bis(dimethylamino)-thiobenzophenone (EK)
2-Nitrofluorene (EK)
4-Nitrophthalimide (EK)
p-Quaterphenyl (EK)
p-Terphenyl (EK)
Tetrabromophthalic anhydride (EK)
Tetraiodophthalic anhydride (EK)
Mixed thujaplicins (CZ)
1,3,5-Triphenylbenzene (A)

Metal-Organic Compounds

Palatine fast blue BNOA (GD)
Palatine fast orange R (GD)
Palatine fast blue BNOA-CF (GD)
Heliogen blue BNF pdr. (GD)
Heliogen SBLA pdr. (GD)
Fastusol blue LRRU (GD)
Fastusol blue LFBGL (GD)
Palatine fast black WANA conc. (GD)
Fastusol grey LGL (GD)
Fastusol turquoise blue LGA (GD)
Suprelan olive green BA (GD)
Suprelan Bordeaux NB-CP (GD)
Suprelan yellow NR-CF (GD)
Palatine fast red GREW (GD)
Palatine fast pink BNA high conc. CF (GD)
Palatine fast green BLNA conc. CF (GD)
Suprelan blue NB-CF (GD)
Fastusol blue LR (GD)
Palatine fast blue GGNA extra conc. (GD)
Fastusol brown LBRSA (GD)
Heliogen blue BG pdr. (GD)
Heliogen green GA pdr. (GD)
B-Triphenylborazine (WADC)
N-Naphthylferrocenecarboxamide (WADC)
N-Octadecylferrocenecarboxamide (WADC)
N-Phenyl-N-1-naphthylferrocene-carboxamide (SRI)
N-Phenylferrocenecarboxamide (WADC)
N-(p-Bromophenyl)ferrocenecarboxamide (WADC)
N-(Ferrocenylcarbonyl)phenothiazine (SRI)
Ferrocene (SRI)
Ferrocenylamine benzylurethan (SRI)
Ferrocenylamine (SRI)
N-(Ferrocenylcarboxylethyl)-ferrocenecarboxamide (SRI)
Isomeric C-(Ferrocenylcarbonyl)-phenothiazine (SRI)
N-(Ferrocenylcarbonyl)morpholine (SRI)
N,N-Bis(ferrocenylcarboxyethyl)-ferrocenecarboxamide (SRI)

N-Ferrocenylcarbonyl-N,N-dicyclohexylurea (SRI)
N-Ferrocenylferrocenecarboxamide (SRI)
Isopropoxytitanium acylate (TRSOA) (DP)
Triethanolamine titanate-N-linseed acid salts (TAT-L-211) (DP)
N,N,N',N'-Tetramethylbenzidine (EK)
p,p'-Methylenebis(N,N-dimethylaniline) (EK)
Uracil (EK)
Indanthrene blue RSA pdr. (indanthrone) (GD)
Ammeline (ACC)
1,12-Benzoperylene (A)
Phenyl sulfide (EK)
Isonicotinic thionamide (WADC)
1,4,2-Benzoselenazin-3-one (WADC)
5-Ethyl-10,10-diphenylphenasilin (WADC)
Phenyl selenide (EK)
Barium diphenylamine sulfonate (GFC)
5-(p-Dimethylaminobenzylidene)-rhodanine (EK)
4,4'-Dihydroxydiphenylsulfone (MCC)
Arochlor 5442 (MCC)
Arochlor 1268 (MCC)
Alizarine blue SAP CF (GD)
Alizarine direct blue AGG (GD)
Indanthrene blue BCSA pdr. (GD)
Indanthrene navy blue BRA pdr. (GD)
Alizarine supra sky RA (GD)
Alizarine cyanone RC (NAD)
Lake scarlet R (NAD)
Indanthrene blue BCS pdr. (GD)
Tetrachlorohydroquinone (EK)
Pyrene (UCC)
Pyrene (EK)
Anthracene (EK)
Phenanthrene (UCC)
Acenaphthene (EK)
Triphenylene (A)
N,N'-Di-2-naphthyl-p-phenylenediamine (EK)

p-Bromo-N,N-dimethylaniline (EK)
2,5-Diphenyloxazole (EK)
Fluoranthene (RTC)
Fluoranthene (UCC)
N-(5-Chloro-2-methyl-4-nitrophenyl)-benzenesulfonamide (A)
Benzanilide (EK)
Naphthalene (BA)
Graphite (AGB)
Perylene (A)
Benzo[a]pyrene (EK)
Dibenz[a,h]anthracene (EK)
Tri-p-tolyl thiophosphate (SRI)
Octoylene glycol titanate (OGT-31) (DP)
Triethanolamine titanate-N-stearate (TAT-S-211) (DP)
Iron octoate (GE)
Diphenyltin oxide (SRI)
Triphenylphosphorus (MTC)
Tetraphenyltin (MTC)
Copper complex of mixed thujaplicins (SRI)
Triphenylantimony (MTC)
Sodium tetraphenylboron (BA)
Tetraphenylidboroxide (A)
p-(Acetoxymercuri)aniline (EK)
Di-p-tolylmercury (EK)
Triphenylstibine (EK)
Triphenylarsine (EK)
Triphenylbismuthine (EK)
Tetraphenyltin (MTC)
Cobalt kojate (SRI)
Zinc kojate (SRI)
Lead kojate (SRI)
Tin kojate (SRI)
Manganese kojate (SRI)
Iron kojate (SRI)
Triisopropanolamine borate (SRI)
Triethanolamine borate (SRI)
2-Nitroso-1,8-dihydroxy-3,6-naphthalene-disulfonic acid, copper complex (A)

[a] Sources, (A) Aldrich Chemical Co., (ACC) American Cyanamid Co., (AGB) A.G. Busch and Co., (BA) Baker analyzed, (CZ) Crown Zellerbach, (DP) Du Pont, (EK) Eastman Kodak, (GD) General Dyestuff Co., (GE) General Electric, (GFC) G.F. Smith Chemical Co., (MCC) Monsanto Chemical Co., (MTC) Metals and Thermit Corp., (NAD) National Aniline Division, Allied Chemical Co., (RTC) Reilly Tar and Chemical Corp., (SRI) Standford Research Institute, (UCC) Union Carbide Chemicals Co., (WADC) Wright Air Development Center.

Table II. Test Conditions for Fluids

Fluid	Temp., °F.	Time, Hr.	Gas	Washers
G.E. Versilube F-50 silicone	518	48	Air	Cu, Ag, Al, steel, Ti
	550	48	95% N₂ 5 %O₂	Cu, Al, steel Ti, stainless
	700	10	Same	Same
Silane, MLO 57-628	500	48 24	Air	Cu, Ag, Al, steel, Ti
	550	48	95% N₂ 5% O₂	Cu, Al, steel Ti, stainless
	700	10	Same	Same
Paraffinic mineral oil MLO 57-574	500	48 24	Air	Cu, Ag, Al, steel, Ti
Naphthenic mineral oil MLO 57-573	550	48 24 18	95% N₂ 5% O₂	Cu, Al, steel Ti, stainless
Pentaerythritol tetra-caproate, MLO 57-426	500	48	Air	Cu, Ag, Al, steel, Ti

Table III. Solubility of Effective Compounds in F-50 Silicone

Amount of Additive, %	Treatment of Additive[a]			
	1	2	3	4
1,1'-Binaphthyl (A)				
1.00	s	i	i	i
0.50	s	i	i	i
0.20	s	s	s	s
0.10	s	s	s	s
Decacyclene (A)				
0.20	i	i	i	i
0.01	i	i	i	i
1,2-Benzanthracene				
0.50	s	i	i	i
0.20	s	s	s	s
0.10	s	s	s	s
Dinaphthenethiophene (A)				
0.20	i	i	i	i
0.01	i	i	i	i
4,4'-Bis(dimethylamino)-benzophenone (EK)				
0.20	i	i	i	i
0.10	s	i	i	i
0.05	s	s	s	s
Chrysene (EK)				
0.20	i	i	i	i
0.05	s	i	i	i
0.03	s	s	s	s
N,N'-Di-2-naphthyl-p-phenylenediamine (EK)				
0.20	i	i	i	i
0.01	i	i	i	i
Indanthrene Navy Blue BRA powder (GD)				
0.20	i	i	i	i
0.01	i	i	i	i
2,5-Diphenyloxazole (EK)				
1.00	s	s	i	i
0.50	s	s	s	s
0.20	s	s	s	s
0.10	s	s	s	s
Fluoranthene (RTCC)				
1.00	s	s	i	i
0.50	s	s	s	s
0.20	s	s	s	s
Perylene (A)				
0.20	i	i	i	i
0.01	i	i	i	i
Benzo[a]pyrene (EK)				
1.00	s	i	i	i
0.50	s	i	i	i
0.20	s	s	s	s
0.10	s	s	s	s
Dibenz[a, h]anthracene (EK)				
0.20	i	i	i	i
0.01	i	i	i	i
Pyrene (UCC)				
1.00	s	i	i	i
0.50	s	i	i	i
0.20	s	s	i	i
0.10	s	s	s	s
Phenanthrene (UCC)				
1.00	s	s	s	s
0.20	s	s	s	s
Acenaphthene (EK)				
1.00	s	s	s	s
0.20	s	s	s	s
N-Phenylferrocenecarboxamide (WADC)				
0.20	i	i	i	i
0.01	i	i	i	i
1,3,5-Triphenylbenzene (A)				
0.01	i	i		
1,12-Benzoperylene (A)				
0.01	i	i		

[a] 1, Agitated in F-50 silicone fluid at 150° C. (302° F.) with a stream of N₂ for 2 hours; 2, solution held at room temp. for 3 days; 3, then at −65 F. for 3 days; 4, and again at room temp. for 3 days.

ated by kinematic viscosities at 100° and 210° F. Low-temperature solubilities were determined as follows: The additives were agitated for 2 hours in the fluid at 150° C. (302° F.) with a stream of nitrogen; the solution was held at room temperature for 3 days, then at −65° F. for 3 days, and again at room temperature for 3 days. The additives were then evaluated as antioxidants at those concentrations at which they were soluble at −65° F. Low temperature solubilities of several of the effective additives are sufficient to warrant consideration for practical use.

The toxicity factor of some concern was carcinogenic activity. Several of the condensed ring aromatic compounds that are effective antioxidants in F-50 silicone fluid exhibit carcinogenic activity in mice. The potential health hazard to humans working with these compounds as lubricant additives is not known. Certainly caution is advisable.

Results of the solubility tests of effective additives are presented in Table III. The evaluation in F-50 silicone fluid at their −65° F. solubility levels is shown at 518° F. in Table IV, and at 550° F. in Table V. Screening results at the 0.2% level for 48 hours are shown for the effective additives at 518° F. in Table VI, and at 550° F. in Table VII.

At this time, on the basis of these criteria, the most promising additive for F-50 silicone fluid is 1,2-benzanthracene; pyrene is ranked second and acenaphthene third. Fluoranthene, phenanthrene, and 2,5-diphenyloxazole are alternate candidates for fourth rank. Acenaphthene was especially effective at 550° F. at a 1.0% concentration. The information on which this selection was made is summarized in Table VIII, which consists of material taken from Tables III through VII. For each of the effective compounds, the following data are presented at 518° and 550° F.: average per cent of viscosity increase at 100° F.; the number of runs on which the average was based; and the appearance of the fluid after the test. These data are given at two concentration levels: the highest concentration at which the additive was soluble at −65° F., and the routine screening level of 0.2%. Tests were run at 518° F. with dry air and at 550° F. with 5% O₂–95% N₂. Tests run at 700° F. with 5% O₂–95% N₂ are not included, because the additives were deleterious under these conditions.

Although the reproducibility of results was poor, there was little difficulty in picking the effective compounds. However, the rankings are arbitrary, because many additional data are obviously necessary to delineate the variables involved. In the mechanism study of gelation, the gel time was fairly reproducible, and at least in the case of fluoranthene, gave useful information. For example, the gel time of F-50 silicone fluid at 518° F. was increased from 10.4 hours for the unprotected fluid to 78 hours by 0.2% fluoranthene, and to 194 hours by 2.0% fluoranthene. Apparently, part of the fluoranthene was degraded, and part

of it was swept out of solution. It would be useful to know whether relatively small amounts of additives added at intervals rather than in a single portion would prolong the gel time. Synergistic possibilities exist, and should be investigated. The additives tested represent only a very small part of the known, condensed aromatic ring system. The effects of substituents on these ring systems have not been studied.

On the basis of effectiveness and solubility, the best additive is benzo[a]pyrene. Unfortunately, it is a powerful carcinogenic agent in mice. Dibenz[a, h]anthracene is also very effective, though insoluble as well as carcinogenic. The other compounds evaluated are classified as negative or weakly active carcinogens in mice.

In comparing severity of conditions at 518° F. using air, with those at 550° F. using 5% O_2–95% N_2, conflicting evidence was noted. Gelation resulted at the end of 48-hour runs under both sets of conditions, but the gel was dis-

Table IV. Most Effective Compounds at Highest Concentration at Which They Were Soluble at −65° F. in F-50 Silicone, Evaluated at 518° F., 1 Liter Dry Air per Hour for 48 Hours

Additive	Concn., %	Fluid Wt. Change, G.	Viscosity[a] At 100° F. Cs.	At 100° F. % Change	At 210° F. Cs.	At 210° F. % Change	Acid No.	Fluid after Test	Al	Cu	Steel	Stainless steel	Ti	Ag
Phenanthrene (UCC)	1.00	−0.5	90	50	36	80	2.1	Clear, yel.	+0.16	+0.28	+0.14	+0.02	+0.08	...
	1.00	−0.5	107	66	35	75	1.6	Clear, yel.	+0.16	+0.14	+0.08	+0.02	...	...
Acenaphthene (EK)	1.00	−0.2	81	35	27	35	1.8	Opaque brn.	+0.08	+0.04	+0.10	+0.06	+0.02	...
	1.00	−0.4	89	46	29	45	2.0		+0.04	+0.20	−0.02	...	0.00	+0.10
4,4'-Bis(dimethylamino) be nzophenone (EK)	0.05	−0.7	...	...	...	...	...	Yel. gel.	...	...	...	...	...	...
Chrysene (EK)	0.03	−0.8	121	101	38	90	1.7	Clear yel.	+0.06	0.00	+0.04	−0.16	+0.08	...
	0.03	−0.5	123	105	48	140		Clear yel.	+0.20	+0.06	+0.02	+0.02	+0.06	...
Fluoranthene (RTC)	0.50	−0.3	69	15	29	45	1.8	Dk. yel.	+0.16	−0.12	+0.12	+0.04	+0.08	...
	0.50	−0.3	125	108	34	70	1.9	Clear dk. yel.	+0.08	−0.30	+0.06		+0.04	+0.24
2,5-Diphenyloxazole (EK)	0.50	−0.4	...	...	...	...	...	Dk. br. gel						
	0.50	−0.4	...	...	...	...	...	Brn. gel						
2,5-Diphenyloxazole (EK)	0.35	−0.3	113	83	37	85	1.0	Clear dk. yel.	−0.02	−0.32	+0.02	...	0.00	+0.16
	0.35	−0.3	487	711	177	785	0.9	Clear dk. yel.	−0.02	−0.24	+0.08	...	−0.02	+0.30
	0.20	−0.1	97	61	28	40	1.4	Clear yel.						
	0.20	−0.3	119	98	33	65	1.2	Clear yel.						
Pyrene (UCC)	0.10	−0.5	73	21	28	40	1.6	Clear lt. br.	+0.06	0.00	+0.08	+0.08	+0.06	...
	0.10	−0.4	88	46	29	45	1.9	Clear dk. yel.	−0.04	−0.10	+0.16	...	+0.02	+0.24
1,1'-Binaphthyl (A)	0.20	−0.6	94	56	30	50	1.9	Clear yel.						
1,2-Benzanthracene (A)	0.20	0.0	70	28	25	25	2.3	Clear yel.						
	0.20	−0.4	77	28	25	25	2.3	Clear yel.						
Benzo[a]pyrene (EK)	0.20	−0.3	69	15	24	20	2.2	Clear dk. brn.						
	0.20	−0.1	72	20	24	20	2.1	Clear dk. brn.						

[a] Viscosity of F-50 silicone fluid before test was 60 cs. at 100° F. and 20 cs. at 210° F.

Table V. Most Effective Compounds at Highest Concentration at Which They Were Soluble at −65° F. in F-50 Silicone Evaluated at 550° F., 1 Liter Dry 5% O_2–95% N_2 per Hour for 48 Hours

Additive	Concn. %	Fluid Wt. Change, G.	Viscosity At 100° F. Cs.	At 100° F. % Change	At 210° F. Cs.	At 210° F. % Change	Acid No.	Fluid after Test	Al	Cu	Steel	Stainless steel	Ti
1,1'-Binaphthyl (A)	0.20	−2.6	...	...	...	...	...	Bk. brn. gel.					
1,2-Benzanthracene (A)	0.20	−0.5	137	118	44	120	2.6	Dk. brn.					
	0.20	−0.7	133	111	42	110	4.2	Dk. brn.	+0.10	−0.04	+0.10	+0.02	+0.02
Benzo[a]pyrene (EK)	0.20	−0.5	89	41	29	45	4.4	Dk. brn.					
	0.20	0.0	86	36	28	40	4.7	Dk. brn.	+0.30	−0.30	+0.08	+0.06	+0.04
4,4'-Bis(dimethylamino) benzophenone (EK)	0.05	−1.1	...	...	...	...	4.7	Brn. gel.					
	0.05	−2.0	...	...	...	...	...	Dk. brn. gel					
Chrysene (EK)	0.03	−1.9	...	...	...	...	...	Dk. brn. gel					
	0.03	−4.6	...	...	...	...	...	Dk. brn. gel					
	0.50	−0.6	...	...	...	...	...	Dk. brn. gel					
Fluoranthene (RTC)	0.50	−1.1	...	...	Insufficient sample		...	Viscous brn.					
	0.50	−0.9	>500	>733			1.6	Clear dk. brn.					
Pyrene (UCC)	0.10	−1.0	201	235	33	65	2.0	Clear brn.	+0.6	−0.52	+0.02	0.00	+0.02
	0.10	−0.9	431	618	249	1145	1.7	Clear dk. brn.					
Phenanthrene (UCC)	1.00	−1.6	...	...	...	...	...	Viscous, brn.					
	1.00	−1.4	...	...	...	...	...	Brn. gel.					
Acenaphthene (EK)	1.00	−0.7	124	106	43	115	2.6	Opaque brn.	+0.10	−0.90	+0.10	+0.08	+0.04
	1.00	−0.6	114	90	39	95	2.5	Opaque brn.					

Table VI. Most Effective Additives at 0.2% Concentration in F-50 Silicone Fluid at
518° F., 1 Liter Dry Air per Hour for 48 Hours

Additive, 0.2% Concn.	Apparent Solubility in Fluid	Fluid Weight Change, G.	Viscosity at 100° F. Cs.	% Change	Acid No.	Fluid after Test	Change in Metals, Mg./Sq. Cm. Al	Cu	Steel	Ag	Ti
1,1'-Binaphthyl (A)	S	+0.1	120	107	1.7	Clear yel.	0.00	-0.78	+0.16	+0.28	...
		-1.0	84	33	1.5	Clear dk. yel.	+0.04	-0.48	0.00	+0.32	-0.06
		-1.1	137	118	1.8	Clear dk. yel.	+3.08	-1.36	+0.86	-4.78	+10.06
Decacyclene (A)	I	-0.6	94	49	1.1	Br.	+0.48	+0.16	+0.30	+0.38	...
		-0.5	120	91	2.7	Opaque brn.	-0.06	-0.20	-0.10	+0.02	-0.20
		-0.7	101	60	2.0	Opaque brn.	-2.82	-1.20	-0.64	+5.42	-9.88
		-0.3	88	40	1.7	Opaque brn.	+0.14	-0.26	+0.06	+0.24	+0.08
1,2-Benzanthracene (A)	S	-0.4	85	35	1.9	Yel.	+0.70	-1.12	+0.24	+0.40	...
		+0.1	73	16	2.2	Clear brn.	+0.06	-2.10	-0.04	+0.18	-0.10
		-0.4	64	2.7	1.8	Clear dk. yel.	+0.28	-0.76	+0.04	+0.20	+0.60
		-0.8	80	27	2.2	Clear dk. yel.	+0.16	+0.36	+0.34	+0.36	+0.06
Dinaphthlenethiophene (A)	I	-0.4	83	33	1.2	Brn.	+0.20	+0.14	+0.22	+0.30	...
		+0.8	73	16	2.2	Opaque brn.	+0.02	-0.52	+0.08	+0.12	+0.02
		-0.4	70	11	1.4	Opaque brn.	+0.12	-0.12	+0.08	+0.10	+0.04
		-0.2	59	- 6	1.9	Clear brn.	+0.12	-0.06	+0.04	+0.08	-0.02
4,4'-Bis(dimethylamino)-benzophenone (EK)	I	-0.9	117	86	1.1	Clear yel.	+0.08	-0.26	+0.12	+0.20	+0.02
		-0.6	193	207	0.8	Clear yel.	+0.06	-0.28	+0.12	+0.24	-0.02
		-1.1	91	44	1.0	Opaque yel.	+0.18	-0.02	+0.16	+0.14	+0.10
		-0.7	155	146	1.2	Clouded yel.	+0.24	-0.14	+0.38	+0.28	...
Chrysene (EK)	I	-1.1	104	65	1.6	Yel.	+0.02	-0.12	+0.08	+0.26	...
		-0.5	108	71	1.4	Clear yel.	+0.16	-0.16	-0.02	+0.22	-0.02
N,N'-Di-2-naphthyl-p-phenylenediamine (EK)	I	-0.4	71	13	0.8	Opaque brn.	+2.66	-0.92	+0.74	-3.14	...
		-0.2	70	11	0.6	Opaque brn.	+0.04	-0.54	+0.10	+0.10	-0.04
Indanthrene Navy	I	-1.2	90	44	2.5	Violet	+0.02	-1.98	-0.02	+0.40	...
Blue BRA Powder (GD)	I	-0.6	136	116	1.8	Clear violet	+0.28	-0.08	+0.06	+0.30	0.00
2,5-Diphenyloxazole (EK)	S	-1.1	162	157	1.5	Yel.	+0.02	-0.64	-0.04	+0.26	...
		-0.5	66	5	1.5	Clear yel.	+0.06	-0.46	+0.04	+0.22	+0.06
		-0.4	84	33	1.7	Clear yel.	+0.06	-0.28	+0.06	+0.24	+0.06
		-0.5	69	9.8	1.7	Clear yel.	+0.02	-0.42	+0.02	+0.20	0.00
		-0.1	97	61	1.4	Clear yel.	...	...	...	...	...
		-0.3	119	98	1.2	Clear yel.	...	...	...	...	...
Fluoranthene (RTCC)	S	-0.7	88	40	1.8	Clear yel.	+0.02	-0.78	0.00	+0.36	-0.40
		-0.4	187	197	1.5	Clear yel.	+0.08	+0.12	+0.08	+0.42	+0.02
		-0.7	117	85	1.2	Clear yel.	+0.06	+0.22	+0.28	+0.38	0.00
		-0.8	108	73	2.7	Clear yel.	+0.06	-0.24	0.00	+0.22	+0.02
Fluoranthene (UCC)		-0.5	82	30	2.4	Clear yel.	+0.04	-0.02	+0.08	+0.26	+0.02
Perylene (A)	I	-0.3	79	25	2.1	Clear red	+0.08	-0.06	+0.10	-0.02	-0.04
	I	-0.2	73	16	3.1	Clear brn.	+0.02	-0.20	+0.04	+0.10	+0.02
		-0.3	73	16	2.8	Clear brn.	+0.08	+0.04	0.00	+0.14	+0.04
Benzo[a]pyrene (EK)	S	-0.4	76	20	2.1	Clear red	+0.04	+0.34	+0.08	+0.16	0.00
		-0.4	72	14	3.0	Clear brn.	+0.06	-0.32	+0.10	+0.08	+0.02
		-0.3	73	16	2.8	Clear brn.	+0.04	+0.22	+0.04	+0.12	+0.02
Dibenz[a, h]anthracene (EK)	I	-0.6	71	13	2.3	Clear yel.	+0.12	+0.28	+0.06	+0.18	0.00
		-0.3	58	- 7.6	3.2	Clear light brn.	+0.06	-0.18	+0.08	+0.10	+0.02
		0.0	76	21	2.9	Clear light brn.	+0.06	+0.20	+0.02	+0.12	0.00
Pyrene (EK)	S	-0.1	89	41	2.5	Clear brn.	+0.06	-0.42	+0.04	+0.22	+0.02
Pyrene (UCC)	S	-1.8	91	43	2.5	Clear brn.	+0.04	-0.06	+0.08	+0.26	0.00
Phenanthrene (UCC)	S	-1.1	108	60	2.0	Clear yel.	+0.26	-0.36	+0.08	+0.32	0.00
		-0.7	81	28	2.7	Clear yel.	+0.08	-0.84	+0.06	+0.24	+0.02
		-1.1	137	118	2.1	Clear yel.	+0.12	-0.10	+0.04	+0.06	+0.02
Acenaphthene (EK)	S	-0.5	113	79	2.8	Clear light brn.	+0.10	+0.36	+0.08	+0.32	+0.02
		-0.9	146	132	2.5	Clear light brn.	+0.02	+1.24	+0.06	+0.40	+0.02
N-Phenylferrocene-carboxamide (WADC)	I	-0.9	70	11	0.3	Opaque brn.	+0.02	-0.52	+0.06	+0.02	0.00
		-0.3	69	9.8	0.3	Clear brn.	+0.08	-2.42	+0.08	+0.10	+0.04
		-0.7	139	121	1.0	Opaque brn.	+0.12	-0.12	+0.12	+0.20	+0.02

colored at the higher temperature. Furthermore, additives effective at the lower temperature were not effective at the higher. However, the gel time of the untreated fluid at 518° F. was 10.4 hours; at 550° F. it was 28 hours.

The only metal-organic compound tested during this program that showed activity—i.e., no gelation after 48 hours in F-50 silicone fluid at 518° F.—was N-phenylferrocenecarboxamide. Its deficiencies for practical purposes are its insolubility and its tendency [in common with all the ferrocene compounds synthesized (1) and tested] to leave a sediment. Iron octoate at a concentration of 0.006% iron, was reported by Nielsen (6) to be an antioxidant for F-50 fluid at 500° F. Tests here at 500° F. with 1 liter of air

per hour for 48 hours, showed that unprotected F-50 fluid increased in viscosity by 232% (determined at 100° F.); iron octoate in the recommended concentration held the viscosity increase under the same conditions to 60%. However, at 518° F., at the end of a 48-hour period, the fluid containing iron octoate was gelled.

Silane Fluid MLO 57-628. This fluid (supplied by WADC) is octadecyl tri-n-decylsilane. It was screened at 500° F. with dry air, and at 550° and 700° F. with a mixture of 5% O_2-95% N_2. The unprotected fluid was badly degraded after 48 hours at 500° F. with dry air. It bumped and crackled severely during the runs, absorbing oxygen and splitting out water. During the first 2 hours, 55% of the

Table VII. Effective Aromatic and Heterocyclic Compounds Evaluated as Additives in F-50 Silicone Fluid at 550° F., 1 Liter Dry 5% O_2–95% N_2 per Hour for 48 Hours[a]

Additive, 0.2% Concn.	Apparent Solubility in Fluid	Fluid Wt. Change, G.	Viscosity At 100° F. Cs.	Viscosity At 100° F. % Change	Viscosity At 210° F. Cs.	Viscosity At 210° F. % Change	Acid No.	Change in Metals, Mg./Sq. Cm. Al	Change in Metals, Mg./Sq. Cm. Cu	Change in Metals, Mg./Sq. Cm. Steel	Change in Metals, Mg./Sq. Cm. Stainless steel	Change in Metals, Mg./Sq. Cm. Ti
Pyrene (UCC)	S	−1.3	398	533	133	565	3.3	+0.12	−0.66	+0.08	+0.02	+0.02
		−0.5	278	339	83	315	2.3	+0.20	−0.92	+0.18	+0.04	+0.02
1,2-Benzanthracene (A)	S	−0.5	137	118	44	120	2.6					
		−0.7	133	111	42	110	4.2	+0.10	−0.04	+0.10	+0.02	+0.02
Dinaphthylenethiophene (A)	I	0.0	92	62	30	50	3.9					
		0.0	88	40	29	45	4.6	+0.14	−1.20	+0.08	+0.06	+0.04
Decacyclene (A)	I	−0.5	323	414	90	350	2.4					
		−0.8	too viscous to measure									
Perylene (A)	I	−0.5	109	71	36	80	3.4					
		−0.3	160	154	33	65	3.7	+0.34	−0.12	+0.08	+0.04	0.00
Dibenz[a, h]anthracene (EK)	I	−1.1	184	192	57	185	2.7					
		−0.9	178	154	55	175	3.0	+0.08	+0.54	+0.04	+0.04	+0.06
Benzo[a]pyrene (EK)	S	−0.5	89	41	29	45	4.4					
		0.0	86	36	28	40	4.7	+0.30	−0.30	+0.08	+0.06	+0.04

[a] Appearance of fluid after all tests was dark brown and opaque.

Table VIII. Average per Cent Viscosity Increase at 100° F.

(Number of runs and appearance)

Additive Concentration Is Highest Concentration at Which It Was Soluble at −65° F.

Additive	518° F.[a]	Additive concn., %	550° F.[b]	Additive Concn., 0.2% 518° F.[a]	Additive Concn., 0.2% 550° F.[b]
I 1,2-Benzanthracene	22 (2)	0.2	115 (2)	20 (4)	115 (2, opaque)
II Pyrene	34 (2, dk. yel.)	0.1	427 (2)	42 (2)	113 (2, opaque)
III Acenaphthene	41 (2, opaque, brn.)	1.0	98 (2, opaque)	105 (2, light brn.)	Very viscous (1)
IV Phenanthrene	58 (2)	1.0	Gel (2)	68 (3)	Gel (1)
V Fluoranthene	97 (2)	0.5	Very viscous (2)	85 (5)	Gel (2)
VI 2,5-Diphenyloxazole	Gel (2, brn.)	0.5	Gel (2)	51 (4)	Gel (1)
VII 1,1′-Binaphthyl	56 (1)	0.2	Gel (3)	86 (3)	Gel (1)
VIII Benzo[a]pyrene	18 (2, dk. brn.)	0.2	39 (2)	16 (3)	38 (2, opaque)
IX Dibenz[a, h]anthracene	...	<0.01	...	12 (3, light brn.)	123 (2, opaque)
X Dinaphthylenethiophene	...	<0.01	...	14 (4, opaque, brn.)	Gel (2)
XI Perylene	...	<0.01	...	19 (3, brn.)	113 (2, opaque)
XII Chrysene	103 (2)	0.03	Gel (2)	68 (2)	Gel (1)
XIII Decacylene	...	<0.01	...	60 (4, opaque, brn.)	>500 (2, opaque)
XIV 4,4′-Bis(dimethylamino)-benzophenone	Gel (1)	0.05	Gel (2)	120 (4)	Gel (1)
XV Indanthrene Navy Blue BRA powder	...	<0.01	...	80 (2, violet)	Gel (1, violet)
XVI n-Phenylferrocene-carboxamide	...	<0.01	...	47 (3, opaque, brn.)	Gel (1, black)
XVII 1,3,5-Triphenylbenzene	...	<0.01	...	720 (2)	...
XVIII 1,12-Benzoperylene	...	<0.01	...	30 (2, opaque, brn.)	...

[a] All samples clear and yellow except as noted.
[b] All samples dark brown except as noted.

oxygen supplied was absorbed; during the remainder of the run, 30% was absorbed. This represents 2.22 moles per mole of fluid in 24 hours, or 0.094 mole per mole per hour based on a flow rate of 1 liter per hour and a molecular weight of 705. Additives were screened over 24-hour periods because of poor reproducibility of viscosity readings after 48 hours. The average viscosity increase for the unprotected fluid at the end of 24 hours was 129% (100° F.). None of the additives screened at concentrations of 0.2 to 2.0% afforded any improvement.

Somewhat less degradation was caused by 5% O_2–95% N_2 at 550° F. than by dry air at 500° F.; the average viscosity increase for the unprotected fluid after 24 hours at 550° F. was 70% (100° F.). An average of 84% of the oxygen in the inlet gas was consumed by 20 grams of the fluid during a 24-hour run. This represents 1.21 moles of O_2 per mole of fluid over a 24-hour period or 0.0504 mole per mole per hour.

Infrared spectra of untreated silane fluid, and of the fluid after 24 hours at 500° F. with 95% N_2–5% O_2, are presented in Figure 1. The striking features are the appearance of a carbonyl absorption peak at 5.80 microns and increased absorption in the 9- to 10-micron region after oxidation. The former could be due to an acid, ester, aldehyde, lactone, or ketone. The increased acid number of the fluid shows acid formation; yet other carboxylic absorption bonds expected in the 3- to 4-micron region were not observed. The reason may simply be that the high molecular weight acids remaining in the fluid do not have an absorption intense enough in the latter region to be recorded; materials with lower molecular weights were volatilized out, and polymeric materials were insoluble. The strong absorption in the 9- to 10-micron region shown by the oxidized fluid could be at least partially accounted for by Si—O bonds resulting from oxidation of the Si—C bonds. There was no indication of SiO—H bonds in the 3-micron region. The peak at 4.75 microns ascribed to an Si—H bond of an impurity was removed by oxidation.
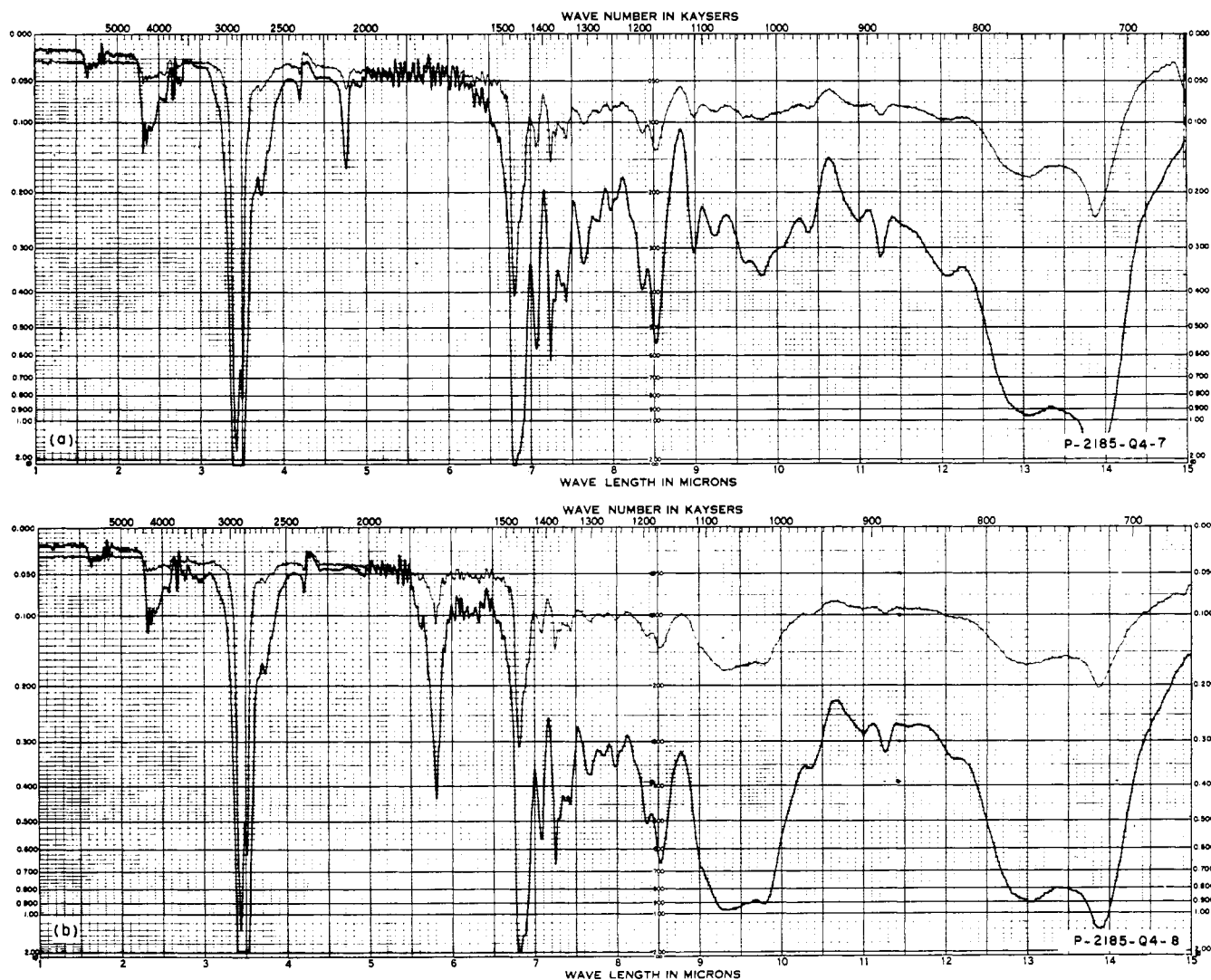
Figure 1. Infrared spectrum of silane fluid MLO 57-628

a. Before test   b. After 24 hours at 550° F. with 5% O₂–95% N₂

Some of the 9- to 10-micron absorption undoubtedly arose from oxidation of the Si—H bond.

To determine the petroleum ether–insolubles formed, including material charred on the test surfaces and on the washers, the following procedure was used: The entire assembly of tube, fluid (20 grams) and washers was weighed to within 0.10 gram. After the oxidation run, the assembly was again weighed, and the fluid was decanted (after removing the inlet tube and washers) into a centrifuge tube which was then centrifuged for 5 minutes and decanted. Twenty-five milliliters of petroleum ether was poured down the sides of the test tube; then the inlet tube and washers were replaced and allowed to soak for 5 minutes. The petroleum ether was decanted onto the residue in the centrifuge tube, which was again centrifuged and decanted. The test tube assembly was allowed to dry and was reweighed. After 24 hours at 550° F. with 5% O₂–95% N₂, the charred material amounted to 3.5%; the centrifuge tube residue was 0.5%.

At 700° F. with 5% O₂–95% N₂, silane fluid MLO 57-628 showed good stability over a period of 10 hours. Average viscosity increase (100° F.) was only 16% (3 runs). The fluid was darkened, but there was very little charred material on surfaces and only several milligrams of petroleum ether–insolubles in the fluid. Fluid weight loss would have been high without condensers because active refluxing occurred. None of the additives screened showed any beneficial effect.

Paraffinic Mineral Oil MLO 57-574. At 500° F. with dry

air, paraffinic oil MLO 57-574 underwent extreme degradation in 48 hours. Even after 24 hours, it was degraded to a very viscous tar, and extensive coking occurred on the tube walls. None of the additives screened were effective in ameliorating this deterioration.

Naphthenic Mineral Oil MLO 57-573. This oil from WADC was screened at 550° F. with 5% O₂–95%·N₂. On the basis of viscosity increase and appearance, oxidative degradation of this fluid was more severe than that of silane fluid MLO 57-627. At the end of 48 hours at 550° F. with 5% O₂–95% N₂, naphthenic mineral oil MLO-573 was an extremely viscous, black, charred tar. After 24 hours, the mineral was black and charred on the walls of the tube, although still fluid enough so that viscosities could be determined (the average viscosity increase for three runs without additives was 161%). Even after 18 hours, the fluid was badly darkened and charred deposits were noted on the walls (the average viscosity increase for two runs without additives was 111%). None of the additives tested at a concentration of 2.0% retarded degradation.

Pentaerythritol Tetracaproate MLO 57-426. Pentaerythritol tetracaproate (Heyden Newport Chemical Corp.) was screened at 500° F. with dry air for 48 hours. Degradation was very severe. The fluid bumped and crackled explosively, and split out water. The exit gases had a strong odor of caproic acid. At the end of the run, most of the fluid samples were black viscous tars with high acid contents. None of the additives tested retarded degradation.

MECHANISM OF PROTECTION OF A SILICONE FLUID

Various phenomena involved in the gelation of the fluid at 518° F. in a stream of dry air were studied in order to elucidate the mechanism of this process and its inhibition in the presence of fluoranthene. Fluoranthene (Union Carbide Chemical Co., recrystallized from ethyl alcohol) was chosen from among the condensed-ring aromatic compounds because of its efficacy, solubility, noncarcinogenic character, and detectability by ultraviolet spectrum.

APPARATUS AND PROCEDURE

In each experiment, six 20-ml. samples of fluid were heated in tubes immersed in a bath maintained at 518° F. The hot fluid was brought to gelation by bubbling a stream of dry air through it at a rate of 1 liter per hour until loss of mobility was observed. In inhibited oxidations, the amount of fluoranthene added to the fluid was 0.2% weight per volume—i.e., 50 mg. per 20-ml. sample. These studies were carried out in the apparatus described for the screening of antioxidants. The system was modified in that the metal washers were removed from the bottoms of the inlet tubes, and the water-cooled condensers were removed from the tops of the sample tubes. (The viscosity increase during a 48-hour period, for both protected and unprotected fluids, was not affected by these changes). A short L-shaped exit tube was attached to the top of sample tube to carry away the off-gases, which were then combined in a manifold and led into a trap cooled to −75° F. with a dry ice–acetone mixture.

The volatile products present in the exit gases from both unprotected silicone fluid and fluid containing 0.2% fluoranthene were identified and determined quantitatively. The presence of formaldehyde in the gas stream was noted at once by its odor and by the condensation of solid formaldehyde polymers on the cooler portions of the apparatus. Formaldehyde evolution and the time required for gelation were the main indications of the rate and extent of oxidation. The amount of formaldehyde formed in an experiment was determined as the total of solid polymer and gaseous formaldehyde. The gaseous formaldehyde was collected in the cold trap along with the other condensable components of the gas stream. The contents of the cold trap (warmed to room temperature) consisted of a white solid (formaldehyde polymers), an organic layer, and an aqueous layer. The aqueous layer contained formic acid and small amounts of formaldehyde. The organic layer consisted of a mixture of cyclic siloxanes containing dissolved 1,2,4,5-tetrachlorobenzene. In experiments in which the silicone fluid was protected by 0.2% of added fluoranthene, unchanged fluoranthene was also found dissolved in the siloxane mixture, along with its oxidation product, 9-fluorenone-1-carboxylic acid.

Removal of the condensate from the various parts of the system was required for determining its weight and composition. Petroleum ether was added to the contents of the cold trap, and the organic and aqueous layers were removed separately by pipetting. The cold trap and the solid product remaining in it were rinsed with a 1:1 mixture of ether and petroleum ether to remove any remaining soluble organic material. Any aqueous droplets adhering to the trap or its solid contents were removed by rinsing with dry tetrahydrofuran. The solid which remained was insoluble formaldehyde polymer; it was allowed to dry and finally was removed mechanically and weighed. Similarly, the other parts of the apparatus in which volatile products had deposited, the exit tubes and the manifold, were rinsed with the ether–petroleum ether mixture to remove soluble organic material. Rinsing with tetrahydrofuran again removed any aqueous material which adhered to these parts of the system. The insoluble formaldehyde polymer which remained behind was allowed to dry, removed mechanically, and weighed by difference.

All the tetrahydrofuran rinses were combined and added to the aqueous layer from the cold trap. The resulting solution was analyzed for water, formic acid, and formaldehyde. Water was determined by Karl Fischer titration; all results were corrected for a tetrahydrofuran blank determined simultaneously. Formic acid and formaldehyde were determined by polarography. The reliability of this method was checked with a synthetic mixture of similar composition. The amount of monomeric formaldehyde found in the aqueous tetrahydrofuran solution was only 5 to 8% of the total in these experiments, the remainder being deposited as solid polymer. Formic acid must have been the only acid present, because the amount determined by polarography agreed with the total acid content determined by titration with base.

All the ether rinses were combined and added to the organic layer from .the cold trap. The combined ether solution was washed with water, and the aqueous wash solution was analyzed for formaldehyde and formic acid by polarography. The amounts found were from 1 to 9% of the total formic acid and less than 1% of the total formaldehyde. The ether solution obtained in experiments using silicone fluid protected with 0.2% fluoranthene was yellow. This color was removed by extraction with 1% aqueous sodium hydroxide. The yellow material was isolated after acidification of the basic extracts and was identified as 9-fluorenone-1-carboxylic acid, melting point 190°, softening at 184° F., by comparison of the infrared spectrum with that of an authentic sample (3), melting point 199–201°, softening at 190° F. About 10 mg. of 9-fluorenone-1-carboxylic acid (4% yield) was obtained from the fluoranthene used in a single experiment (six 20-ml. samples of fluid, each containing 40 mg. of fluoranthene). The air oxidation of fluoranthene to 9-fluorenone-1-carboxylic acid was verified by heating fluoranthene at 518° F. in a stream of air for 93 hours; the ketoacid was formed in 0.3% yield.

The extracted ether solution, which now contained only neutral, water-insoluble products, was dried and evaporated to an oily residue from which crystals separated on standing. In the experiments in which unprotected silicone fluid was used, the residue consisted mainly of tetrachlorobenzene and a mixture of cyclic siloxanes. When the silicone fluid had been protectected with 0.2% fluoranthene, unchanged fluoranthene was also present. The presence of cyclic dimethylsiloxanes was verified by examining the infrared spectrum of the residue from the ethereal filtrate. Neither tetrachlorobenzene, nor fluoranthene in experiments containing additive, was present in sufficient amount to interfere with the siloxane spectrum in the infrared. It was not possible to ascertain the nature of the siloxanes present, because members of the homologous series of cyclic dimethylsiloxanes have very similar infrared spectra (9). Occasional tetrachlorophenyl groups in the siloxanes were indicated by maxima at 242, 297, and 306 mμ in the ultraviolet absorption spectra.

1,2,4,5-Tetrachlorobenzene and fluoranthene, when it was present, were separated from the siloxane mixture by chromatography of a pentane solution on silica gel. Tetrachlorobenzene was eluted with the solvent front. Pentane solutions containing from 1 to 10% ether were used to elute fluoranthene and most of the siloxanes. Although the tetrachlorobenzene and fluoranthene obtained were still contaminated with small amounts of the oily siloxanes, these compounds could be quantitatively determined by comparing the ultraviolet absorption maxima at 296 mμ for 1,2,4,5-tetrachlorobenzene and at 361 mμ for fluoranthene with those of standard solutions.

After separating the condensable products of the silicone oxidation, the off-gases from the cold trap were passed through a drying tube and then through an Ascarite tube

Table IX. Gel Time and Formaldehyde Evolution from F-50 Silicone Fluid at 518° F.

	Unprotected Silicone Fluid, 20.0 G.		Silicone Fluid, 20.0 G., Dry Air	
	Dry air	95% N_2–5% O_2	0.2% fluoranthene	2.0% fluoranthene
Gel time, hr.	10.4 ± 0.4	32.5 ± 1.1	78 ± 12	194 ± 5
HCHO evolved per 20 g. samples (bubbler method), mg.	282 ± 16	208 ± 27	364 ± 14	283 ± 20
Av. rate, mg./hr.	27	6.4	4.7	1.5
Moles HCHO per mole silicone	1.40	1.03	1.82	1.40
HCHO evolved per 20 g. samples (cold trap method), mg.	322		377	
Av. rate, mg./hr.	31		4.8	
Moles HCHO per mole silicone	1.60		1.86	

for absorption of carbon dioxide. The amount of carbon dioxide was measured by the weight increase of the Ascarite tube. Carbon monoxide was identified and determined by infrared analysis of the gas stream. Oxygen content was measured with a Beckman oxygen meter. The sample tubes were weighed before and after oxidation to determine the weight loss of the fluid.

In another series of experiments, formaldehyde evolution alone was determined. The gaseous formaldehyde was collected in water bubblers attached directly to the exit tubes from each sample. Results were obtained from unprotected fluid, and from fluid containing 0.2 and 2.0% fluoranthene. A single run, passing a 95% N_2–5% O_2 mixture through unprotected fluid, was made to evaluate the effects of reducing oxygen concentration.

The gelled fluid from experiments using added fluoranthene was exhaustively extracted with chloroform to remove the fluoranthene remaining in the gel. The amount of unchanged fluoranthene was determined by ultraviolet analysis of the chloroform solution. Small amounts of 9-fluorenone-1-carboxylic acid, amounting to a 3% yield from the fluoranthene originally added, were obtained from basic extracts of the chloroform solution.
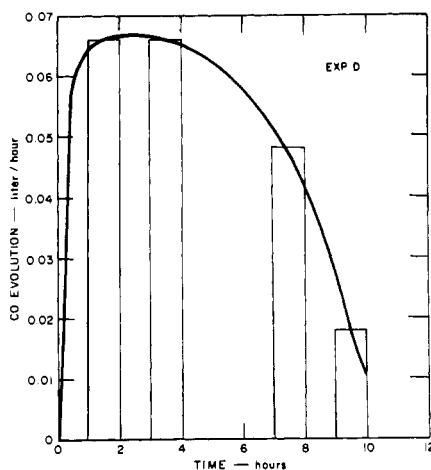

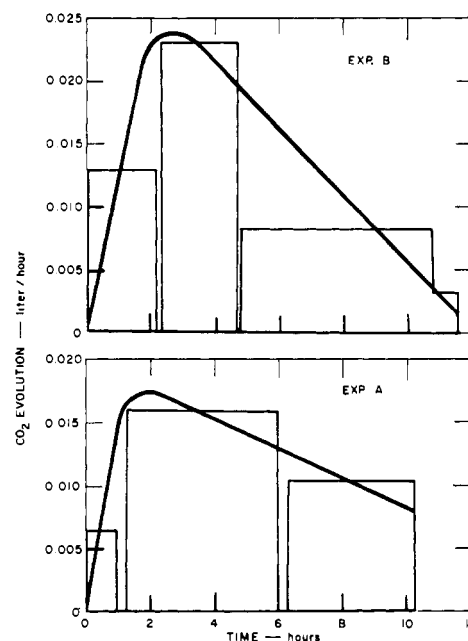Figure 2. Carbon monoxide evolved from unprotected silicone fluid

Figure 3. Carbon dioxide evolved from unprotected fluid

Table X. Oxidation of Silicone Fluid to Gel Point at 518° F.

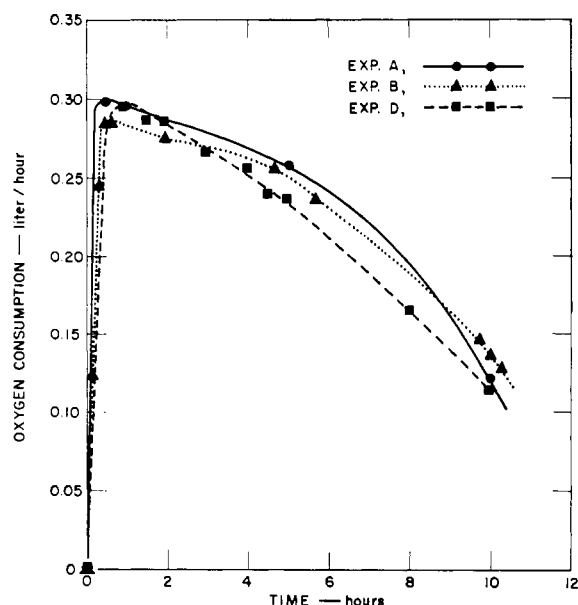|	Silicone Fluid without Additive					Silicone Fluid Containing 0.2% Additive				
Experiment	A	B	C	D	Av.	E	F	G	H	Av.
Wt. fluid, g.	120.6	120.6	120.4	120.5	120.5	120.9	122.0	120.4	121.2	121.1
Fluoranthene added, g.	None	None	None	None	None	0.240	0.240	0.240	0.240	0.240
Gel time, hr.	10.2	10.9	10.2	10.2	10.4	72	73	70	70	71
HCHO, g.	1.90	1.94	1.96		1.93	2.23	2.31	2.23		2.26
HCOOH, g.	0.722	0.538	0.637		0.63	0.422	0.376	0.65		0.48
H_2O, g.		0.98	0.91		0.94	1.97	2.21			2.09
CO, g.				0.60	0.60				0.75	0.75
CO_2, g.	0.233	0.249			0.241	0.044	0.100		0.097	0.80
Tetrachlorobenzene, g.	0.080	0.105			0.092		0.098	0.088		0.093
Siloxanes, g.	1.59	1.88			1.79	2.94	3.67	3.15		3.25
Fluoranthene recovered, g.										
In condensate	...	...	...	...	...	0.059	0.075	0.088		0.074
In gel	...	...	...	...	...			0.060	0.026	0.043
Total condensable products, g.	6.63	6.27	6.50		6.47	8.03	8.93	9.81		8.92
Total volatile products, g.					7.31					9.75
Wt. loss of fluid, g.	3.7	3.1	3.7		3.5	3.85	5.28	6.12		5.08
Over-all wt. increase, g.					3.8					4.67
Metered O_2 uptake, g.	3.10	3.26		2.85	3.07		4.80		4.64	4.72
% of total available	18.7	18.5		17.5	18.2		4.1		4.1	4.1

Figure 4. Oxygen consumed by unprotected silicone fluid

RESULTS

The gel times and amounts of formaldehyde evolved under a variety of conditions are compared in Table IX. The presence of 0.2% fluoranthene increased the gel time about sevenfold over that of unprotected fluid; 2.0% fluoranthene increased the gel time nearly 20-fold; reducing oxygen content to 5% increased gel time threefold. The amount of formaldehyde evolved up to the gel time, however, remained remarkably constant over the range of conditions used. Or, put another way, the rate of formaldehyde evolution was decreased by factors that increased the gel time—i.e., additives or lower oxygen concentration. The variations in amount of formaldehyde evolved may be within experimental limits of error. At any rate, these variations are small compared with the large changes in gel time.

Table X presents the results obtained from oxidative gelation of unprotected fluid and of fluid containing 0.2% fluoranthene. The gram quantities of the various products formed and amounts of oxygen consumed up to the gel point in individual experiments using 6 samples of fluid are listed along with the average values. Figures 2, 3, and 4 present the rate vs. time curves on unprotected fluid for carbon monoxide evolution, carbon dioxide evolution, and oxygen consumption. Figures 5, 6, and 7 present the corresponding curves for fluid containing 0.2% fluoranthene. The following molar ratios of the volatile products from 1 mole of silicone fluid were calculated from the averages in Table X.

Volatile Products	Molar Ratios	
	Without additive	With 0.2% additive
HCHO	1.60	1.86
HCOOH	0.34	0.26
H_2O	1.29	2.88
CO	0.52	0.67
CO_2	0.14	0.045
Tetrachlorobenzene	0.0106	0.0105
Methyl groups cleaved	2.60	2.83

The number of methyl groups cleaved per molecule of silicone fluid was calculated by adding up the molar ratios of the carbon-containing products from the oxidation of methyl groups. This calculation involves only the reasonable assumption that all the products of methyl cleavage were volatilized and determined. The number of methyls removed was only slightly larger (2.83) in the presence of the additive than for unprotected fluid (2.60), although the

time was increased sevenfold. Each molecule contains an average of 82 methyl groups (6); thus about $\frac{1}{30}$ of the methyl groups were lost:

	Unprotected Fluid	Protected Fluid
$\dfrac{\text{Methyls cleaved/molecule}}{\text{Total methyls/molecule}}$	$\dfrac{2.60}{82} = \dfrac{1}{32}$	$\dfrac{2.83}{82} = \dfrac{1}{29}$

The greatest differences between the two situations were in the amounts of water and carbon dioxide formed, and in the weights of cyclic siloxanes volatilized (Table X). In no case, however, did the change approach the ratio of gel times.

The number of moles of oxygen consumed per mole of fluid up to gel point, as determined by metering the oxygen content of the exit gases, can be checked in two ways. Although the fluid itself undergoes a weight loss during the oxidation due to loss of volatile products, there is an over-all weight increase when all the products are determined. This increase must be due only to the oxygen taken up by the fluid, and its magnitude must be equivalent to the amount of oxygen. Another check can be obtained by adding up the number of oxygen atoms which appear in the products of the reaction from 1 mole of silicone fluid. This amounts to all
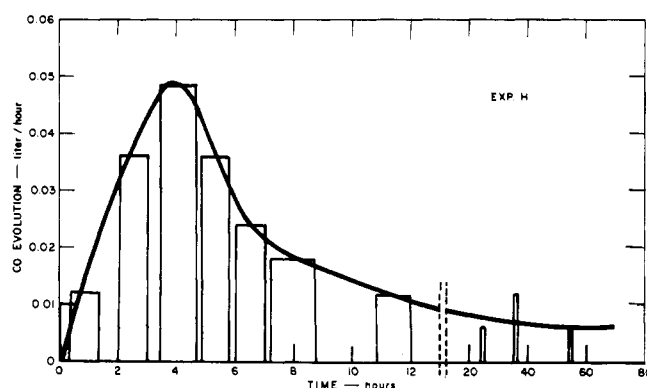

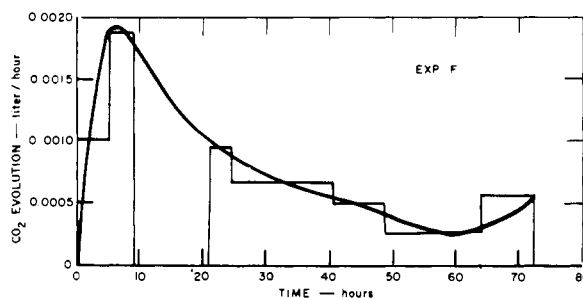Figure 5. Carbon monoxide evolved from silicone fluid with 0.2% fluoranthene

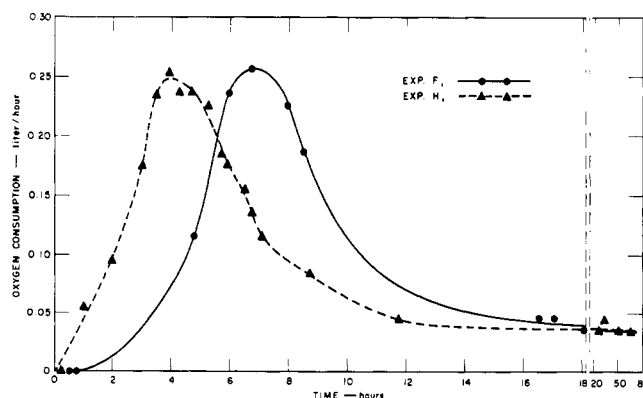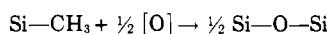Figure 6. Carbon dioxide evolved from silicone fluid with 0.2% fluoranthene

Figure 7. Oxygen consumed by silicone fluid with 0.2% fluoranthene

the oxygens in the volatile products plus ½ an oxygen atom for each methyl group cleaved, on the assumption that each methyl group removed from a silicon atom is replaced by a siloxane link.

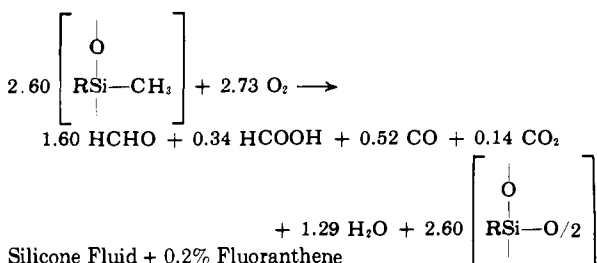$$Si—CH_3 + \frac{1}{2} [O] \rightarrow \frac{1}{2} Si—O—Si$$

The total number of oxygen atoms is then equal to twice the moles of oxygen consumed. The moles of oxygen consumed by 1 mole of silicone fluid determined by these three methods are compared as follows.
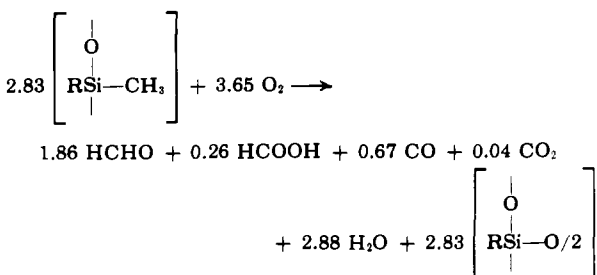
	Oxygen Consumed	
	Unprotected fluid	Protected fluid
Metered O₂ uptake	2.39	3:63
Calcd. from weight increase	2.96	3.61
Calcd. from $\dfrac{O\ atoms\ in\ products}{2}$	2.83	3.72
Av.	2.73 ± 0.22	3.65 ± 0.04

The data permit the stoichiometric relation among the repeating units of silicon fluid, oxygen consumed, and products formed to be defined as follows:

Silicone Fluid without Additive

$$2.60 \begin{bmatrix} O \\ | \\ RSi—CH_3 \\ | \end{bmatrix} + 2.73\ O_2 \longrightarrow$$

1.60 HCHO + 0.34 HCOOH + 0.52 CO + 0.14 CO₂

$$+ 1.29\ H_2O + 2.60 \begin{bmatrix} O \\ | \\ RSi—O/2 \\ | \end{bmatrix}$$

Silicone Fluid + 0.2% Fluoranthene

$$2.83 \begin{bmatrix} O \\ | \\ RSi—CH_3 \\ | \end{bmatrix} + 3.65\ O_2 \longrightarrow$$

1.86 HCHO + 0.26 HCOOH + 0.67 CO + 0.04 CO₂

$$+ 2.88\ H_2O + 2.83 \begin{bmatrix} O \\ | \\ RSi—O/2 \\ | \end{bmatrix}$$

The equation for fluid without additive is unbalanced by an excess of 1.3 hydrogen atoms on the left; the equation for protected fluid has an excess of 1.5 hydrogens on the right. These imbalances represent 15 to 20% of the total hydrogen and may be due to accumulation of experimental error.
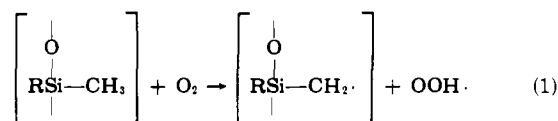
DISCUSSION

In spite of the sevenfold increase in gel time, there was little difference in the over-all chemical change between the normal gelation process and that inhibited by the presence of 0.2% fluoranthene. In particular, the extent of methyl cleavage in the two situations was nearly the same. That this is probably true under the other conditions that were explored briefly was suggested by the relative constancy of formaldehyde evolved up to gel point as presented in Table IX. Undoubtedly gelation depends on cleavage of methyl groups from the fluid, which leads to cross linking of the silicone molecules. Tetrachlorobenzene is a very minor product of the oxidation process, and the loss of tetrachlorophenyl groups (one from 100 silicone molecules) could in no way account for gelation of the fluid. The additive seems only to delay oxygen pickup, methyl cleavage, and

cross linking, rather than to change the nature of the chemical reactions involved. This delaying action must occur before cleavage of the Si—C bond, because rates of oxygen consumption and methyl cleavage are affected.
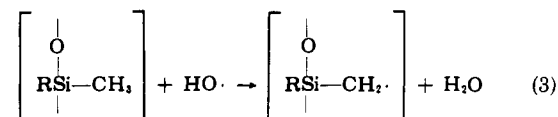
It is reasonable to assume that the cross links formed are merely additional siloxane bonds between the silicone molecules, because no new types of bonds were detected by infrared comparison of unoxidized and gelled fluid. (The spectra of unoxidized fluid and gelled fluid were almost superimposable.) Oxygen consumption, calculated on the basis of one siloxane cross link replacing two methyl groups, checked with the other methods.

The rates at which the oxidation processes occurred, as observed by rate of oxygen consumption, require some explanation. For instance, the considerable decrease in rate of oxygen consumption from an initial maximum observed with unprotected fluid (Figure 4), and checked by the rates of carbon monoxide and carbon dioxide evolution (Figures 2 and 3), is rather surprising. The two most likely explanations are formation of an oxidation inhibitor as a product of the oxidation reaction, or loss of a highly oxidation-susceptible substance present in the fluid which would have been oxidized rapidly at first and used up. No data are available to distinguish between these alternatives. There is no obvious explanation for the different shape of the rate curve (Figure 7, checked by Figures 5 and 6) obtained with fluid containing 0.2% fluoranthene. Nevertheless, it seems possible that the delayed maximum, followed by a decrease to a steady, low rate of oxidation, might be related to the continuous sublimation of fluoranthene out of the fluid during the oxidation.
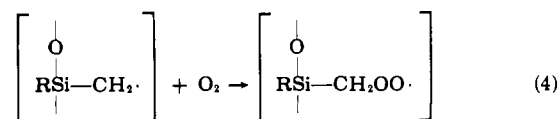
It is fairly certain that the oxidation process was initiated by reaction of oxygen with the methyl groups in the silicone fluid to form reactive free-radical intermediates; these underwent further reactions leading to gelation. This is supported by analogy with hydrocarbon oxidations which have been studied extensively. Furthermore, passing a stream of nitrogen through the fluid at 518° F. showed that the process was not initiated by heat alone; there was no viscosity increase in 27 hours, and the formaldehyde evolved was negligible (6 mg. from 120 grams of fluid). A postulated initiation step, analogous to those involved in hydrocarbon oxidations, may be expressed as follows:
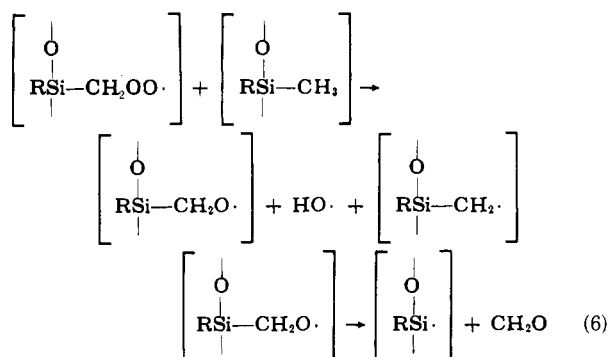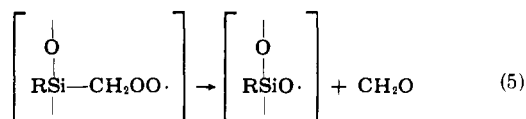
$$\begin{bmatrix} O \\ | \\ RSi—CH_3 \\ | \end{bmatrix} + O_2 \rightarrow \begin{bmatrix} O \\ | \\ RSi—CH_2· \\ | \end{bmatrix} + OOH· \qquad (1)$$

The peroxide radical can initiate similar reactions

$$\begin{bmatrix} O \\ | \\ RSi—CH_3 \\ | \end{bmatrix} + HOO· \rightarrow \begin{bmatrix} O \\ | \\ RSi—CH_2· \\ | \end{bmatrix} + 2\ HO· \qquad (2)$$

$$\begin{bmatrix} O \\ | \\ RSi—CH_3 \\ | \end{bmatrix} + HO· \rightarrow \begin{bmatrix} O \\ | \\ RSi—CH_2· \\ | \end{bmatrix} + H_2O \qquad (3)$$

Presumably attack by a single oxygen molecule can result in the removal of a hydrogen atom from four methyl groups. Oxygen would be highly reactive toward the radical produced and would add to it rapidly at 518° F.

$$\begin{bmatrix} O \\ | \\ RSi—CH_2· \\ | \end{bmatrix} + O_2 \rightarrow \begin{bmatrix} O \\ | \\ RSi—CH_2OO· \\ | \end{bmatrix} \qquad (4)$$

The adduct could then rearrange or react further in a number of ways to give formaldehyde and siloxy radicals.

$$\left[\begin{array}{c} \text{O} \\ | \\ \text{RSi—CH}_2\text{OO·} \\ | \end{array}\right] \rightarrow \left[\begin{array}{c} \text{O} \\ | \\ \text{RSiO·} \\ | \end{array}\right] + \text{CH}_2\text{O} \qquad (5)$$

$$\left[\begin{array}{c} \text{O} \\ | \\ \text{RSi—CH}_2\text{OO·} \\ | \end{array}\right] + \left[\begin{array}{c} \text{O} \\ | \\ \text{RSi—CH}_3 \\ | \end{array}\right] \rightarrow$$

$$\left[\begin{array}{c} \text{O} \\ | \\ \text{RSi—CH}_2\text{O·} \\ | \end{array}\right] + \text{HO·} + \left[\begin{array}{c} \text{O} \\ | \\ \text{RSi—CH}_2\text{·} \\ | \end{array}\right]$$

$$\left[\begin{array}{c} \text{O} \\ | \\ \text{RSi—CH}_2\text{O·} \\ | \end{array}\right] \rightarrow \left[\begin{array}{c} \text{O} \\ | \\ \text{RSi·} \\ | \end{array}\right] + \text{CH}_2\text{O} \qquad (6)$$

Siloxane linkages could be formed in many ways from two silyl radicals and oxygen, or from a siloxy and a silyl radical. Alternatively, radical displacement reactions are known, and displacement of a partially oxidized methyl group by a siloxy radical might also be a route to siloxane links. If the siloxane links are formed between two silicone polymer molecules, the result is the cross linking which causes gelation. If an intramolecular siloxane bond is formed the product is a cyclic siloxane.

From the magnitude of the ratio of methyl groups cleaved to molecules of fluoranthene present (90/1), obviously one molecule of the additive must function at many sites. It is postulated that the additive acts by forming a transient adduct between the polycyclic aromatic molecule and the radical intermediates of the oxidation reaction. There are several analogies for the formation of adducts between aromatic hydrocarbons and radical intermediates reported in the literature (2, 4, 8). The nature of the bonding forces in such adducts is debatable. It has been reported that the phenomenon of "methyl affinity" of aromatic compounds involves the entry of the unpaired electron of the methyl radical into the lowest unoccupied molecular orbital of the aromatic molecule, without binding the methyl to a particular carbon atom (5). Perhaps a similar situation prevails in the adduct between aromatic additives, such as fluoranthene, and certain radical intermediates of the oxidation reaction of the silicone fluid. Dissociation of the adduct after a time by a reversal of the addition process would regenerate the aromatic compound and the free radical, which would then follow a normal but delayed reaction route to gelation of the fluid.

The fact that about 50% of the fluoranthene added was unchanged at the gel point, along with 7% of an oxidation product, 9-fluorenone-1-carboxylic acid, supports this hypothesis. This same compound and recovered fluoranthene, along with some carbonaceous degradation products, were also obtained from the air oxidation of molten fluoranthene at 518° F. Apparently the fate of the fluoranthene is no different when mixed with the silicone fluid.

The most likely steps to be affected by the additive in the reaction scheme presented would be steps 2, 3, 5, and 6. The additive could have no influence on step 1, the initiation step, which does not involve radical reactants. Step 4 would probably proceed at too fast a rate to be affected. Operation of the additive in delaying the actual

cross-linking processes after cleavage of the Si—C bond cannot be important in this system. If the major protecting influence were exercised in this part of the system, methyl cleavage from protected fluid would proceed unimpeded, although gelation would be delayed, and the amount of methyl cleavage for the protected fluid should be increased over that of the unprotected fluid in proportion to the ratio of gel times. As it is, there is only slightly more Si—C splitting when the fluid contains fluoranthene. If the major protecting influence were solely in steps 2 and 3, the amounts of water formed from the protected and unprotected fluids should be the same. On the contrary, more water is obtained from protected runs, but not as much more as would be predicted by the ratio of gel times if no delaying action occurs in steps 2 and 3. Therefore, the delaying action of the additive must occur both in steps 2 and 3 and in steps 5 and 6. Of these, steps 2 and 6 involve initiation of other chains, besides furthering the process already initiated.

How formic acid, carbon monoxide, and carbon dioxide are formed from methyl-group oxidation is not clear. Formic acid and carbon dioxide might be formed in secondary oxidation processes. Further oxidation of formaldehyde could lead to either formic acid or carbon dioxide and water. Carbon dioxide could also be formed from carbon monoxide. For these reasons, the decreased evolution of carbon dioxide from protected fluid cannot be definitely correlated with the mechanism of silicone oxidation and its inhibition.

A considerably larger weight of cyclic siloxanes was obtained from the protected than from the unprotected fluid. The explanation for this may be complicated by the factors involved in the formation of cyclic siloxanes. The cyclic siloxanes are formed to a certain extent as a result of oxidative degradation. This amount should be comparable for protected and unprotected fluid. Cyclic siloxanes may also be produced by rearrangement and depolymerization of the silicone molecules, brought about by heat or traces of acid. The amount in this case should depend only on the time involved. That both these processes are involved is suggested by the fact that the weight of cyclic siloxanes is considerably increased for the protected fluid, but not to be extent predicted by the ratio of gel times.

ACKNOWLEDGMENT

LITERATURE CITED

(1) Acton, E.M., Silverstein, R.M., J. Org. Chem. 24, 1487 (1959).
(2) Chamberlain, G.H.W., Walsh, A.D., Trans. Faraday Soc. 45, 1032 (1949).
(3) Forrest, J., Tucker, S.H., J. Chem. Soc. 1948, p. 1141.
(4) Levy, M., Swarc, M., J. Am. Chem. Soc. 77, 1949 (1955). Additional references.
(5) Matsen, F.A., J. Chem. Phys. 24, 602 (1956).
(6) Nielsen, J.M., General Electric Co., private communication, 1958.
(7) Scott, W.W., "Standard Methods of Chemical Analysis," N.H. Furman, ed., 5th ed., Vol. II, p. 1844, Van Nostrand, New York, 1939.
(8) Walsh, A.D., Trans. Faraday Soc. 45, 1043 (1949).
(9) Wright, M., Hunter, M.J., J. Am. Chem. Soc. 69, 803 (1947).
(10) Wright Air Development Center, Tech. Rept. 54-576, Part I, February 1955.
(11) Ibid., 55-448, Part III, May 19, 1956.
(12) Ibid., 55-449, Part III, Appendix I, May 1956.