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D_2 -meta-CARBORANE-SILOXANES. VI.
OXIDATIVE STABILIZATION OF VULCANIZATES WITH FERRIC OXIDE

by

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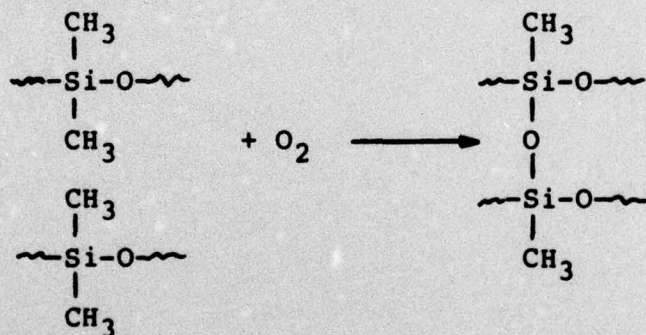
D₂-m-CARBORANE-SILOXANES. VI. OXIDATIVE STABILIZATION OF VULCANIZATES WITH FERRIC OXIDE

ABSTRACT: Ferric oxide produced from iron pentacarbonyl was evaluated as an oxidative stabilizer in D₂-m-carborane-siloxane and polydimethylsiloxane vulcanizates. The results indicate a significant improvement in efficiency compared to powdered ferric oxide. Thus a carborane-siloxane vulcanizate retained elastomeric properties after 1000 hours in air at 315°C.

The practical upper use temperature for carborane-siloxane vulcanizates were evaluated by heat aging samples at 340° and 370°C.

INTRODUCTION

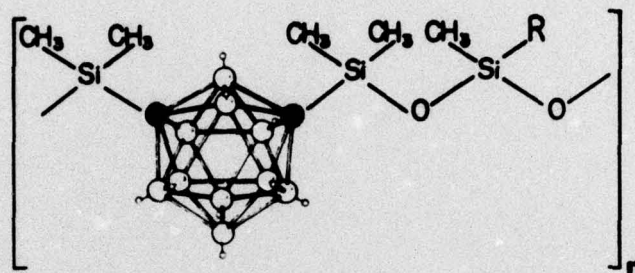
The thermal aging of conventional polydimethylsiloxanes in air has been represented as a cross-linking oxidation reaction.¹ The mechanism of this oxidation is believed to be a diverging, free-radical chain reaction, initiated by direct attack of oxygen on the methyl groups of the siloxane polymer.^{1,2} This increase in cross-link density of silicone vulcanizates during thermal aging in air leads to a loss of useful properties.



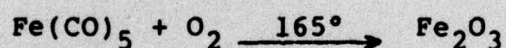
Stabilizers and antioxidants are important in elastomer formulations.³ Iron and other redox metal compounds are used to stabilize polydimethylsiloxanes in order to prolong their service life.⁴ The stabilizing by ferric oxide has been postulated to occur by the destruction of the propagating species, $\text{R}^\bullet$, of a free radical chain reaction.



The incorporation of the decacarborane moiety into the siloxane backbone significantly enhances the thermal stability.⁵⁻⁸ This paper describes investigations on the thermal



and thermo oxidative stability and use of ferric oxide stabilizers in carborane-siloxanes. Furthermore, Neale and Pines have reported an improved preparation of ferric oxide from iron pentacarbonyl which is apparently soluble in silicone oils and results in better antioxidant efficiencies.⁹



This soluble ferric oxide has been evaluated in carborane-siloxanes and polydimethylsiloxane vulcanizates, and found to be highly efficient in stabilizing these elastomers.

EXPERIMENTAL

Linear, high molecular weight stocks were prepared by the reaction of bis-ureidosilanes with carborane disilanol. This technique has been described elsewhere.^{7,10} D₂-m-carborane-dimethyl/diphenylsiloxane (67/33 mole %) was used in these studies. Compounding and vulcanization are similar to standard silicone conditions.^{7,11} Dicumyl peroxide was used as the curing agent. The cure cycle was 125°C for 20 minutes and

150°C for 30 minutes, followed by post cure at 180°-200°C for 18 hours, then 12 hours at 315°C. The polydimethylsiloxanes were post cured only at 180-200°C. Heat aging studies were carried out in an air circulating oven.

Soluble Ferric Oxide

Incorporation of soluble ferric oxide into stocks was carried out in a well ventilated fume hood by cautiously adding, via syringe, iron pentacarbonyl to a hot solution of the stock in a suitable solvent (tetrahydrofuran, chlorobenzene, *o*-dichlorobenzene, etc). Evaporation of the solvent and simultaneous air oxidation of the iron pentacarbonyl results in polymer containing soluble ferric oxide. Vacuum drying removes traces of solvent and leaves a reddish transparent polymer which was suitable for compounding and curing. The iron content was determined by atomic absorption after ashing. Up to 50% of the iron pentacarbonyl was converted in solution to ferric oxide.

RESULTS AND DISCUSSION

Carborane-siloxane polymers exhibit excellent thermal stability as measured by thermal gravimetric analysis.⁶ However, it was desired to gain an understanding of the thermal stability of vulcanizates and define a time-temperature profile.

Heat Aging at 315°C

Vulcanizates with and without powdered ferric oxide were heat aged in air and nitrogen at 315°C. The results appear in Tables I and II.

In air, the specimens without ferric oxide undergo rapid oxidative cross-linking. After 150 hours at 315°C the modulus increases from 530 to 154,000 psi, the tensile strength increases from 510 to 1,490 psi and the elongation at break decreases from 100 to 1%. This cross-linking is corroborated by the volume change in benzene.

The samples containing powdered ferric oxide exhibit much less tendency to cross-link during heat aging in air at 315°C. For example, after 150 hours the modulus increases from 533 to 1800 psi, the elongation at break decreases from 100 to 45%, and the tensile strength shows no significant change. Thus, ferric oxide is an effective oxidative stabilizer for carborane-siloxanes.

In nitrogen both samples during heat aging exhibit a decrease in modulus, tensile strength, and elongation at break. These results indicate that the vulcanizates are undergoing bond cleavage during heat aging. This is corroborated by the increased swelling in benzene.

Decomposition in nitrogen is attributed to the cleavage of the cross-link moieties on the polymer backbone. A key experiment was performed in which D₂-carborane-siloxane stock was heat aged in nitrogen at 315°C for 150 hours. The molecular weight ($\bar{M}_w$) after heat aging (192,000) was almost identical to the molecular weight before heat aging (198,000). Clearly, the stock backbone is not undergoing any significant amount of bond cleavage at 315°C. The loss of mechanical properties

observed by heat aging vulcanizates in nitrogen must be due to thermal breaking of cross-link bonds.

The property change occurring in air at 315° must be the result of a combination of thermal cleavage of cross-link moieties and oxidative bond forming reactions.

Heat Aging at 340° and 370°C

To define the practical upper use temperature for D₂-carborane-siloxane, vulcanizates were aged in air at 340° and 370°C. The results appear in Tables III and IV. There is a more rapid loss of mechanical properties at 340° and 370°C than at 315°C. The property changes are consistent with increased cross-linking during heat aging.

Heat aging D₂-carborane-siloxane stock in nitrogen for 24 hours at 340°C resulted in partial thermal cross-linking as indicated by the reduced solubility in chloroform and other good solvents. At 370° the stock is totally cross-linked. These results suggest that at these temperatures the carborane-siloxane is undergoing bond formation reactions at a faster rate than bond cleavage.

Conventional silicones undergo reversion reactions under these conditions.

Soluble Ferric Oxide

Soluble ferric oxide is a highly effective oxidative stabilizer for silicones. The effectiveness of soluble ferric oxide was compared against powdered ferric oxide in carborane-siloxane vulcanizates. Samples containing 0.25 phr soluble ferric

oxide and 0.25 phr powdered ferric oxide were heat aged in air at 315°C up to 1000 hours. The results appear in Table V.

After 50 hours the sample with 0.25 phr powdered ferric oxide became very rigid. The modulus increased from 508 to 141,000 psi and the elongation at break decreased from 190 to 2%. At a 0.25 phr level, powdered ferric oxide is not an effective stabilizer. At the 2.5 phr level it is effective (Table I).

However, with 0.25 phr soluble ferric oxide, the sample retained most mechanical properties after 1000 hours at 315°C. The modulus increased from 536 to 3300 psi, the tensile strength remained essentially constant, and the elongation at break decreased from 220 to 15%. This clearly demonstrates the superior efficiency of soluble ferric oxide as an oxidative stabilizer for carborane-siloxanes.

Polydimethylsiloxane

The usefulness of soluble ferric oxide has been demonstrated in silicone fluids and carborane-siloxane vulcanizates. Its effect in polydimethylsiloxane vulcanizates was studied. Samples containing 0.25 phr powdered and soluble ferric oxide were heat aged in air. The data appear in Table VI.

The sample with powdered ferric oxide showed a rapid loss of properties after 25 hours at 315°. The sample with soluble ferric oxide exhibited a much better retention of properties.

CONCLUSIONS

Ferric oxide is an effective oxidative stabilizer for carborane-siloxanes. The use of soluble ferric oxide results in a substantially improved efficiency for stabilization for carborane-siloxanes and polydimethylsiloxanes. Indeed a carborane-siloxane sample retained properties after 1000 hours at 315°C in air.

ACKNOWLEDGMENT

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TABLE I

MECHANICAL PROPERTIES AT 25°C
AFTER HEAT AGING IN AIR AT 315°C^a

Aging time, hrs	Young's modulus, psi	Tensile strength, psi	Elongation at break, %	Volume change, ^b %
No ferric oxide				
0	530	510	100	91
25	1170	365	50	85
50	1520	470	40	70
75	3190	350	20	65
150	154,000	1490	1	20
ferric oxide, 2.5 phr ^c				
0	533	513	100	88
25	922	442	60	94
50	1117	427	55	65
75	1311	485	50	67
150	1813	533	45	68

TABLE II

MECHANICAL PROPERTIES AT 25°C
AFTER HEAT AGING IN NITROGEN AT 315°C^a

Aging time, hrs	Young's modulus, psi	Tensile strength, psi	Elongation at break, %	Volume change, ^b %
No ferric oxide				
0	530	510	100	91
25	457	277	75	105
150	246	180	60	112
ferric oxide, 2.5 phr				
0	533	613	100	88
25	470	520	80	110
50	450	420	60	105
75	420	300	50	104
100	400	200	40	107

^a Polymer 100, Tullanox 500 30, dicumyl peroxide 2.5.

^b ASTM test method D471-72; immersed seven days in benzene at room temperature.

^c Mechanical properties from reference 7.

TABLE III
MECHANICAL PROPERTIES AT 25°C
AFTER HEAT AGING IN AIR AT 343°C^a

Aging time, hrs	Young's modulus, psi	Tensile strength, psi	Elongation at break, %
0	430	740	220
4	460	739	125
16	952	503	50
24	1140	293	30

TABLE IV
MECHANICAL PROPERTIES AT 25°C
AFTER HEAT AGING IN AIR AT 371°C

Aging time, hrs	Young's modulus, psi	Tensile strength, psi	Elongation at break, %
0	430	740	220
4	15,600	839	15
16	b		

^a Polymer 100, Tullanox 500 30, Powdered ferric oxide 2.5, and dicumyl peroxide 2.5.

^b Too brittle to measure.

TABLE V

EFFECT OF FERRIC OXIDE ON MECHANICAL PROPERTIES (25°C)
AFTER HEAT AGING IN AIR AT 315°C^a

Aging time, hrs	Young's modulus, psi	Tensile strength, psi	Elongation at break, %
Powdered ferric oxide, 0.25 phr			
0	508	517	190
50	141,000	1880	2
100	243,000	2050	1
300	Too brittle to measure		
Soluble ferric oxide, 0.25 phr			
0	536	527	220
50	712	434	165
100	855	581	80
300	1240	470	50
600	2000	500	35
1000	3300	457	15

^a Polymer 100, Tullanox 500 30, dicumyl peroxide 1.5.

TABLE VI
 PROPERTIES OF POLYDIMETHYLSILOXANE AT 25°C
 AFTER HEAT AGING IN AIR AT 315°C^a

Aging time, hrs	Young's modulus, psi	Tensile strength, psi	Elongation at break, %	Volume change, % ^b
Powdered Ferric oxide, 0.25 phr				
0	348	820	450	160
25	3022	567	25	53
50	3480	539	20	45
75	4700	522	12	35
150	7500	780	2	10
300	- too brittle to measure			-
Soluble ferric oxide, 0.25 phr				
0	333	704	400	196
25	438	286	180	132
50	661	496	90	116
75	840	300	50	107
150	1080	482	40	97
300	1833	607	12	40

^a Polymer 100, Tullanox 500 30, dicumyl peroxide 2.5.

^b ASTM test method D471-72; immersed seven days in benzene at room temperature.

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