Fluoroalkylene Ether Silicate/Viton GLT Blends: An Approach toward Improved Low Temperature Flexibility

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Synopsis

Low molecular weight fluoroalkylene ether silicate (FES) polymers demonstrating glass transition temperatures of -82° C to -91° C were obtained from the condensation polymerization of fluoroether bisdimethyl carbinols and bis(dimethylamino) methyl vinyl and dimethyl silane derivatives. Peroxide cure reactivity through the pendant vinyl moieties was demonstrated. In an effort to improve the low temperature flexibility of a peroxide curable fluorocarbon elastomer (Viton GLT from Du-Pont), blends were prepared using the FES material as an additive cocuring plasticizer. Temperature retraction tests demonstrated an optimum 5° C (9° F) improvement in low temperature flexibility. The optimum blend formulation employed FES polymers with vinyl cure site concentrations ranging from 2.35 to 2.70 mol %. The optimum blend formulation maintained the strength and low compression set properties of the Viton GLT standard. These properties reflect sufficient cocuring between the FES and Viton GLT components to provide physical properties adequate for o-ring seal application. o-Ring seal evaluations in Freon E6.5 fluid (rod and piston seal tests) demonstrated some seal enhancement and comparable durability to standard Viton GLT o-rings.

The development of elastomers providing improved serviceability for aircraft components such as hydraulic seals is an on-going goal of Air Force research. Fluorocarbon elastomers provide the best overall combination of thermal, oxidative, and hydrolytic stability, abrasion resistance, and high mechanical strength. Their major drawback, lack of low temperature flexibility, has generally precluded their use in wide temperature hydraulic seal applications. However, with the development of Viton GLT® by DuPont, this aspect of fluorocarbon elastomers was substantially improved.

Testing demonstrated static sealing capability of the Viton GLT as low as -46° C.² Our efforts became focused on further improving the low temperature flexibility of the Viton GLT while maintaining all of its other excellent properties. We felt this could be achieved by elastomer blending provided the additive polymer could act as a cocuring reactive plasticizer.

The additive polymer anticipated to fulfill this criteria can be described with respect to its backbone structure as a fluoroalkylene ether silicate:

$$\begin{array}{c|cccc} CH_3 & CH_3 & CH_3 \\ \hline & & & & \\ \hline & & & & \\ \hline & & & & \\ \hline & & C-O-Si-O-C-R_f \\ \hline & & & & \\ \hline & & & \\ CH_3 & R & CH_3 \\ \end{array}$$

R = methyl and/or vinyl
R_f =
$$(CF_2OCF_2)_6$$
, 7, or 8
or
 $-CF_2 - (OCF_2CF_2)_m O - (CF_2)_5 - O - (CF_2CF_2O)_n - CF_2 - m + n = 5 \text{ or } 6$

This structure provided the chemical stability and low temperature flexibility of the fluoroether chain, peroxide cure reactivity at the pendant vinyl site, and hydrolytic stability from steric hindrance imparted by hydrocarbon branching around the hybrid silicate bond.

The fluoroalkylene ether silicate (FES) polymers were obtained by the condensation polymerization of fluoroether bisdimethyl carbinols and appropriately substituted bis(dimethylamino) silane derivatives³:

The vinyl concentration in the polymers was varied by reacting the diol with an appropriate mixture of the bis(dimethylamino) methyl vinyl and bis(dimethylamino) dimethyl silane derivatives.

Throughout the research, the optimum o-ring formulation for Viton GLT developed by DuPont served as a standard for comparison to the blends. TR-10 improvement with minimal sacrifice of any other property was the goal of blend development. Table I gives the Viton GLT standard o-ring formulation and its physical properties. Most blends were prepared with the same components and relative loadings used in the Viton GLT standard. Table II lists the general structures and physical properties of the FES polymers used in the blending studies.

RESULTS AND DISCUSSION

Blend Optimization

Several sets of blend research data were compiled while developing an optimum blend formulation. The effect on blend properties of the following variables was examined: (1) FES vinyl cure site concentration, (2) relative quantities

TABLE I
Viton GLT Standard Formulation and Physical Properties

		COMPO	NENTS (pph lo	adings)	
Viton GLT	Austin Black	MT Black	Ca(OH) ₂	TAICA	Luperco 101XL ^b
	20 0 min @ 177°C h rise to 260°C p		4 260°C (500°F)	4	4
		PHYSI	CAL PROPER	TIES	
T _B [MPa (psi)]	M ₁₀₀ [MPa (psi)]	E _B (%)	Shore A hardness	TR-10 [°C (°F)]	Compression set (%)

78

-29 (-20.2)

15

15.55

(2255)

155

8.76

(1270)

a Triallylisocyanurate.

^b 2,5-Dimethyl-2,5-bis(t-butylperoxy)hexane.

General structure	T_{g}	TGA (20°C/min)	mol % (vinyl)	Designation
$- \left(\begin{array}{cccc} CH_{,3} & CH_{,3} & CH_{,3} \\ & & & \\ C-&O-S_{i}-O-C & R_{r}^{a} \\ & & & \\ CH_{,3} & CH & CH_{,i} \\ & & & \\ CH_{2} & & \end{array} \right)$	-82°C to	10% weight los by 290°C, rapid weight loss >300°C		high-vinyl
$- \begin{pmatrix} CH_{_{3}} & CH_{_{3}} & CH_{_{3}} \\ & & & \\ C-O-Si-O-C-R_{_{f}} \\ & & \\ CH_{_{3}} & R^{b} & CH_{_{3}} \end{pmatrix}$		same as above	0.39-0.62	low-vinyl

TABLE II
Summary of FES Structures and Properties

of Viton GLT/FES, and (3) lower press/post cure temperatures. The essential parameter involved with these variables was the state of cure of the blend compound. To clarify the relationship between cure state and physical properties, the blend data in Table III are presented in four groups (I–IV). Each group illustrates the effect on physical properties of a variation in one condition effecting cure while all other factors effecting cure are held constant. The constants and variation for each group are identified in Table III. The data sets are representative of from four to eight separate runs using each condition specified. The order given also approximates the chronological progression of the blend studies leading up to the optimum formulations in Group IV.

Group I

Blends were first prepared using the high-vinyl FES polymers in 80/20 pph Viton GLT/FES ratios. Strong vulcanizate properties were obtained, but at the prohibitive sacrifice of ultimate elongation, which for o-ring application must be maintained well over 100%. This overcuring was presumably due to the high cure reactivity of the FES vinyl site. Use of more FES only aggravated the problem.

Group II

To prevent overcuring of the blends, FES polymers were used having considerably lower vinyl cure site concentrations. The reduced degree of cure provided good elongation with fairly well-balanced overall properties. Use of more FES again failed to provide improved properties. Use of lower press and/or post cure temperatures seemed particularly attractive as an alternative method to reduce FES cure; thermogravimetric analysis (in air at 20°C/min) of the uncured FES polymers showed a 1–2% weight loss at 260°C, implying the possibility of long-term oxidative degradation during the standard post cure conditions of 24 h at 260°C. Any loss of FES structural integrity would reduce its plasticizing ability.

a $R_f = -CF_2 + OCF_2CF_2 + mO(CF_2)_5 + CF_2CF_2O)_n - CF_{2m+n=5 \text{ or } 6} \text{ or } + CF_2OCF_2 + 6.7 \text{ or } 8.7 \text{ or }$

 $b R \equiv methyl or vinyl.$

TABLE III Blend Data Summary

		Blend properties					
		T_B [MPa (psi)]	M ₁₀₀ [MPa (psi)]	E _B (%)	Shore A hardness	TR-10 [°C (°F)]	Comp. set (%)
Group I							
Constants:	high-vinyl FES						
Maniakian	standard cure cycles						
Variation:	Viton GLT/FES (pph)						
	80/20	14.97		100	87		
		(2170)					
	60/40	5.52		70	87		
		(800)					
Group II							
Constants:	low-vinyl FES						
	standard cure						
Variation:	cycles						
variation:	Viton GLT/FES (pph)						
	80/20	9.55	6.72	170	79	-31.7 (-25)	20.5
		(1385)	(975)				
	70/30	7.69	7.10	107	82		
	60/40	(1115) 5.38	(1030)	105	85	-31.1 (-24)	
	00/40	(780)		105	60	-31.1 (-24)	
		(/					
Group III Constants:	low-vinyl FES						
Constants.	80/20 Viton GLT/FE	S					
	(pph)	~					
Variation:	press and post						
	cure cycles						
	press cure: 60 min						
	@ 149°C	3.79	2.63	550		-30.5 (-22.9)	
	post cure: 24 h	(549)	(381)	000		30.0 (,	
	@ 149°C						
	press cure: 10 min						
	@ 177°C	7.66	6.24	145	78	-32.7 (-26.9)	35a
	post cure: 24 h	(1110)	(905)	2.20	, ,	32 (20.0)	00
	@ 177°C						
Group IV							
Constants:	high-vinyl FES						
	standard press cure 80/20 Viton GLT/						
	FES (pph)						
Variation:	post cure						
	temperature:						
	post cure: 24 h @ 177°C	10.17	8.55	195	. 00	94.9 (90.7)	
	@ 111 C	10.17 (1475)	(1240)	135	82	-34.3 (-29.7)	
	post cure: 24 h						
	@ 204°C	11.45	10.24	125	83	-34.0 (-29.2)	16.1ª
		(1660)	(1485)				

				`
TABLE III	(Continued	trom	previous	page.)

		Blend properties					
		T_B [MPa (psi)]	M ₁₀₀ [MPa (psi)]	E _B (%)	Shore A hardness	TR-10 [°C (°F)]	Comp. set (%)
Gelled High-V Conditions:	inyl FES 80/20 Vitcon GLT/ FES (pph) standard cure cycles						
		15.03 (2180)	14.0 (2030)	130	84	-32.8 (-27.0))

^a Blends from which o-rings were prepared for seal evaluation.

Group III

The combined effect of both low-vinyl FES and lower cure cycle temperature is shown in Group III. Cure temperatures of 149°C or less were inadequate. Use of 177°C cure temperature gave results comparing in some respects favorably with those obtained in Group II, notably TR-10 and modulus.

Group IV

Though demonstrating improved TR-10, the blends in Group III indicated an undesirable compromise of Viton GLT's strength and compression set resistance. In reducing the degree of FES cure, too much was sacrificed in the way of strength and ability to recover from mechanical deformation. A method was needed to increase the blend crosslink density to a point where TR-10, strength, elongation, and compression set resistance could achieve an optimum balance.

High blend strength had been demonstrated in the Group I high-vinyl FES formulations. Use of a lower post cure temperature with the high-vinyl FES was anticipated to provide optimization of strength, elastomeric character, and low temperature flexibility. Blend formulations using an 80/20 pph ratio of Viton GLT to high-vinyl FES and post cure temperature of 177°C and 204°C provided overall optimization of physical properties. Moduli and compression set were fully comparable to the Viton GLT standard. The elongations, though lower, were within satisfactory limits. TR-10's were optimally improved, consistent with the suspected detrimental effect of the 260°C post cure temperature on the FES component.

o-Ring Evaluation

To determine if this improvement in TR-10 could be manifested in a practical hydraulic seal application, o-rings were prepared from two specific blend formulations (see Table III). Test conditions used simulated those that an o-ring would experience in actual hydraulic system application. A recently developed experimental nonflammable hydraulic fluid from DuPont, Freon E6.5, having the structure

$$F = [-CF(CF_3)CF_2O -]_n - CF(CF_3)H, \quad n = 5, 6$$

was used for the hydraulic seal testing. Standard Viton GLT *o*-rings were subjected to identical testing to obtain baseline data for comparison.

Rod seal testing, specifically designed to evaluate the relative wear resistance of seal materials, demonstrated the blend o-rings to be fully comparable to the Viton GLT standard. Total leakage after 100,000 cycles ranged from 0.5 to 2.0 mL (as compared to a 0.3–1.2-mL leakage range for the Viton GLT standard). Appearance of the o-rings after testing was excellent.

Dynamic piston seal testing was used to determine low temperature seal performance. The specific test procedure was designed to evaluate not only the lowest temperature at which effective sealing was obtained, but also the ability of the o-ring to reseal at low temperatures following several excursions to 135° C. Optimum low-temperature dynamic sealing for the blend o-rings was obtained at -37.2° C (-35° F), as compared to -34.4° C (-30° F) for the Viton GLT standard o-rings. This improvement could have been due in part to the greater volume swell of the blend o-rings in the fluid (9%) than Viton GLT (2%); a certain degree of swell generally enhances seal ability, since it can help compensate for compression set taken by the o-ring during service. Overall leakage rates of the blend o-rings after 50,000 cycles including five 135°C excursions (0.2–1.5 mL) were lower than those of the Viton GLT standard (0.7–7.9 mL).

CONCLUSIONS

An important limitation in this research was no doubt the low molecular weight of the FES materials. Higher molecular weight FES could have better dispersion/plasticizing capabilities. More cocuring with the Viton GLT could result in producing greater strength properties.

Results along these lines were obtained from a standard 80/20 pph Viton GLT/gelled high-vinyl FES blend (see Table III). Remarkable data evident here were the very high tensile and particularly modulus values indicating a crosslink density of much greater magnitude than in any ungelled FES blend or the Viton standard compound.

Comparison of the modulus data provides insight to the FES/Viton GLT interaction at the bulk molecular level. The low-vinyl FES blends were cured enough to provide sufficient strength and TR-10 improvement. However, they had an overall diluent effect on the Viton GLT, lowering its crosslink density in relation to the standard Viton GLT compound.

The high-vinyl FES blends reflect a crosslink density comparable to that of Viton GLT. The diluent effect is not present here. Cocuring evidently went further in these blends giving greater strength and, because of increased FES/Viton GLT interaction, better TR-10. These results are qualitatively consistent with the much higher vinyl cure site concentrations used.

For the gelled high-vinyl FES, these interactions apparently occurred but to a much greater magnitude. The key variable would appear to be the molecular weight of the gelled FES (theoretically infinite) compared to the low molecular weight of the ungelled FES materials (0.10–0.15 dL/g inherent viscosity). The gelled FES could provide more entanglement with the Viton GLT giving a more homogeneous system with greater proximity of FES and Viton GLT polymer domains. This greater proximity could increase cocuring between these systems generating higher crosslink density and modulus. Increased cocuring would

insure the plasticizing effect of the FES additive, as reflected in the improved TR-10.

Improvements on this blending approach to fluorocarbon elastomer development, including use of higher molecular weight additive materials, might increase the magnitude of low temperature flexibility obtained. A more difficult problem to approach is providing a greater degree of cure control, providing, in effect, equivalent peroxide reactivity (cure rates) to the Viton and FES systems. This could provide a magnitude of cocuring previously unattained and could make a dramatic difference in resultant physical properties. Synthesis of FES polymers with other peroxide curable pendant groups (i.e., oxymethyl) is a possible approach. The potential of this blend approach is not limited to the FES system; any low T_g polymer compatible with fluorocarbon elastomers might be successfully used, provided it could take part in the curing process.

EXPERIMENTAL

Synthesis

The starting materials for synthesizing the fluoroalkylene ether silicate polymers were prepared as shown below:

$$C - CF_{2} \leftarrow OCF_{2}CF_{2} \xrightarrow{m} O(CF_{2})_{5} - O(CF_{2}CF_{2}O \xrightarrow{n} CF_{2} - C \xrightarrow{O} F$$

$$m + n = 5,6$$

$$= C - R_{f} - C \xrightarrow{O} F$$

$$n = 6, 7, \text{ or } 8$$

$$C - R_{f} - C \xrightarrow{O} C \xrightarrow{(1) 4CH_{3}MgI, \text{ ether}} F$$

$$C - R_{f} - C \xrightarrow{O} C \xrightarrow{(2) H_{3}O^{+}} F$$

$$C - R_{f} - C \xrightarrow{O} C \xrightarrow{(2) H_{3}O^{+}} F$$

$$C - R_{f} - C \xrightarrow{O} C \xrightarrow{CH_{3} CH_{3}} CH_{3}$$

$$C - R_{f} - C \xrightarrow{CH_{3} CH_{$$

The ether diacid fluorides (EDAF's) and dichlorosilanes were prepared and supplied by PCR, Inc., Gainesville, Florida.⁴

The general experimental procedure for preparation of the fluoroether bisdimethyl carbinols follows:

To a 300-mL, three-necked round-bottom flask equipped with a mechanical stirrer, addition funnel (60 mL), and reflux condenser topped with a nitrogen inlet (all glassware dried in oven overnight) was added 1.65 g (70 g-atoms) of Mg turnings. Anhydrous ethyl ether (40 mL) was added to the flask and, under a dry nitrogen blanket, 9.0 g (63 mmol) of iodomethane dissolved in 40 mL ether was added dropwise at a rate sufficient to maintain a mild reflux. After addition of the iodomethane and Grignard formation exotherm, the solution was stirred and heated at mild reflux for 30 min. Then 20 mL of dry F-2-butylfuran was added all at once to the Grignard solution. A solution of an EDAF (10 mmol) in 40 mL of F-2-butylfuran was then added dropwise at ambient temperature to the vigorously stirred solution at a rate sufficient to maintain a mild reflux. A fairly rapid addition rate (ca. 5 drops/s) was satisfactory. After addition of the EDAF solution, the reaction mixture was heated to reflux for 1 h. A dry nitrogen atmosphere was maintained throughout the above procedure.

The white/gray suspension was allowed to stir under N_2 atmosphere at ambient temperature overnight. The next morning, the excess Grignard was quenched by dropwise addition with vigorous stirring of ethanol (15 mL) and H_2O (approx. 10 mL) until the salts took on a granular appearance. This was followed by the addition of HCl (ca. 30 mL, 10%) until two or three clear phases were observed with all salts dissolved. The Freon 113 soluble layers were combined and saved. The aqueous (Freon 113 insoluble) layer was extracted twice with 15-mL Freon 113 and these washings were combined with the previously saved organic layers. The combined organic layers were successively washed with H_2O (2 × 50 ml), saturated NaHCO₃ (1 × 50 mL), and H_2O (1 × 50 mL), and dried over MgSO₄.

After filtering and evaporation, the residue was fractionally distilled *in vacuo* through a 6-in. Vigreaux column to give the final product as a clear, water white viscous liquid. The diol with the structure of:

$$\begin{array}{c|c} CH_3 & CH_3 \\ & \mid & \mid \\ CH_3 & \mid & \mid \\ CH_3 & CH_3 \end{array}$$

had a bp range of 115–117°C at 0.035-mm-Hg pressure. Yields ranged from 65% to 80%. Elemental analysis gave: C 25.43%, H 1.38%. $C_{22}H_{14}F_{32}O_{10}$ requires C 25.23%, H 1.34%. IR (neat) cm⁻¹: 3400 (OH); 3000 (C—CH₃); 1250–1100 (CF₂OCF₂). NMR (C₆F₆—C₆D₆): 1.3 δ (multiplet, CH₃); 2.0 δ (two singlets, OH); integration showed CH₃/OH ratio of 6 to 1.

The experimental procedure for preparation of the bis(dimethylamino) silane derivatives follows:

To a 300-mL, three-necked round-bottomed flask equipped with a low temperature thermometer, a 2-in. magnetic stir bar, and nitrogen gas inlet was added methyl vinyl dichlorosilane (or dimethyl dichloro silane) (0.105 mol) along with 200 mL of dry petroleum ether (bp range $30-50^{\circ}$ C). After purging the system with nitrogen gas, the solution was cooled to -65° C with an n-butanol/dry ice bath. Then, under direct nitrogen flow, dimethylamine (25.0 g, 0.5 mol) was added directly to the stirred solution. The reaction exotherm sent the temperature up to about 0° C. The reaction mixture was cooled back down to -55° C, and then allowed to warm gradually to room temperature.

After filtering the amine salts and removal of the solvent by simple distillation under nitrogen, the residue was distilled through a 6-in. Vigreaux column under nitrogen atmosphere. The products were obtained at 143–145°C and 125–128°C bp, respectively, as clear colorless liquids. Yields ranged from 50% to 75%. Elemental analysis for $C_7H_{18}N_2Si$ gave C 52.58% (53.16% theor), H 11.20% (11.39% theor). IR (neat) cm⁻¹: 3040 (CH olef); 2910 (CH aliph); 2850 (N—CH₃); 1470 (C=C olef); 1420 (N—CH₃); 1250 (Si—CH₃); 980 (CH₂=CH); 790 (Si—C); 740 (CH olef).

The general polymerization reaction procedure for high vinyl FES follows:

To a 50-mL, three-necked round-bottom flask equipped with a 1-in. stir bar, glass extension capped with a rubber septum, a gas inlet adapter, and a reflux condenser topped with a gas outlet leading to an FC-43 bubbler was added the bis(dimethylcarbinol) (6.7 mmol). Dry xylene (20 mL) was added to the flask and, under gentle nitrogen purge, the mixture was heated until solution was obtained (pot temp 85°C). At this point, bis(dimethylamino) methyl vinyl silane (27 mmol, 4.2 g) was added via syringe through the rubber septum. Litmus paper testing of the nitrogen flow over the reaction indicated strong dimethylamine evolution. The reaction was then heated at xylene reflux under direct nitrogen flow for 23 h. At this point, litmus paper indicated negligible dimethylamine evolution and an off-white polymeric precipitate had formed in the bottom of the flask. After decanting the solvent, the crude polymer was air dried, followed by drying under vacuum (0.1 mm Hg) at 80°C overnight. The appearance of the dried polymer ranged from off-white opaque to translucent colorless and had a thick molasses-like consistency.

The low vinyl FES polymers were prepared in identical fashion except that an admixture of bis(dimethylamino) dimethyl silane (18.6 mmol) and bis(dimethylamino) methyl vinyl silane (9.0 mmol) was added to the diol solution. Also, the 23-h reaction temperature used was 115°C. Mol% vinyl concentrations in the resultant polymers ranged from 0.39% to 0.63%. These concentrations were calculated on the basis of comparison of the H NMR relative integration values of the Si—CH₃ versus Si—CH=CH₂ protons.

Inherent viscosities of all FES polymers (HFIP at 30°C) ranged from 0.10 to 0.15 dL/g. Yields ranged from 90% to 95%. T_g and TGA are summarized in Table II. Carbon and hydrogen elemental analysis agreed with the theoretical values in all cases.

IR (neat) cm⁻¹ general: 2990, 2950 (C—CH₃); 1600 (C—C olef); 1100–1000 (Si—O); 800 (Si—C); 1000 (CH—CH₂); 1320–1000 (fluoroether).

Blend Preparation

Little difficulty was encountered preparing the Viton GLT/FES blends. The FES polymers behaved in typical plasticizer fashion, necessitating some variation from the standard procedure for Viton GLT compound preparation.

The FES had to be blended with the raw Viton GLT first. Adding FES to standard Viton GLT compound caused it to crumble, fall off the mill rolls, and never take on again a cohesive character. Initial addition of the FES had to be very slow. However, once the Viton GLT started to accept the FES additive, it could be added more rapidly. Addition of too much FES all at once usually caused the Viton GLT to crumble presumably due to the lubricating effect of

the FES reducing Viton GLT's adhesion to the rolls. However, with time on the mill, a homogeneous system could again be obtained.

Most blends were prepared on a Coastcraft Rubber Micromill (roll size 3 in. \times 1 in. and 3 in. \times 1½ in.) using the following component loadings for the standard 80/20 blend formulation: 0.8 g Viton GLT, 0.2 g FES, 0.2 g Austin Black, 0.1 g MT Black, and 0.04 g each of Ca(OH)₂, TAICA, and Luperco 101XL.

Several larger scale blends from which o-rings were made (as noted in the blending data summary) were prepared on a Thropp Rubber Mill (roll size 8 in. \times 3 in.). The standard 80/20 blend formulation in these cases used 25 g Viton GLT, 6.25 g FES, 6.25 g Austin Black, 3.125 g MT Black, and 1.25 g each of Ca(OH)₂, TAICA, and Luperco 101XL.

The following chart presents the timetable of blend formulation applicable to both large scale and microscale preparations (Table IV).

o-Ring Testing

Both the blend and control Viton GLT o-rings were fabricated into standard 214-size seals (ASTM designation). The rod seal testing procedure included dynamic cycling performance requirements that serve to screen candidate materials. In the test, the rod diameter was slightly increased over that normally used in rod seal testing in order to exert more abrasion on the inside surface of the o-ring. The test conditions were:

Temperature = 135°C (275°F) Pressure (cyclic) = 20.68 MPa (3,000 psi) Stroke length = 7.5 cm (3.0 in.) Number of cycles = 100,000

Backup rings = MS-27595 (Teflon)

For piston seal testing, each seal was initially checked for low temperature leakage at -54°C (-65°F). If the seal leaked, the temperature was raised 2.8°C (5°F) and again checked for sealability. This process continued until the lowest temperature was determined at which a nonleaking seal occurred. This value then became the low temperature sealing limit for this seal material. The test temperature was then increased to 135°C (275°F) and cycling initiated at 3,000 psi, 2-in. stroke, 30 cycles/min. Approximately 10,000 cycles were conducted

TABLE IV
Timetable for Blend Formulation

Operation	Time required	Comments		
Milling of raw Viton GLT	1 min			
Addition of FES to raw Viton GLT during milling	30 min	Initial addition should be done very slowly; gradual but increased addition rate may follow. Rolls used without water cooling		
Addition of Austin Black, MT black, Ca(OH) ₂ , and TAICA	15 min	All these ingredients were weighed, mixed, and added together; water cooling of the rolls aids in dispersion		
Milling stopped and curing ager	nt	•		
Luperco 101XL is weighed				
Addition of curing agent to blend compound	7 min (large scale)	Water-cooling of rolls important to prevent curing on the mill.		
	4 min (microscale)	-		

during this phase, and seal leakage was recorded. Following the high temperature cycling, the temperature was lowered to the lowest temperature that sealing was maintained. A low temperature pressure check was then conducted to assure that sealing was maintained following high temperature cycling. This high temperature cycling phase followed by a low temperature check continued through five cycling phases, accumulating approximately 50,000 cycles. For both the rod and piston seal tests, seal performance was based on leakage criteria, and post test examination of the seals. A more detailed accounting of the rod and piston seal test procedures can be found in Refs. 5–7.

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