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FLUOROALKYLENEETHER SILICATE/VITON GLT BLENDS FOR
HYDRAULIC SYSTEM SEALS: SYNTHESIS, BLENDING, AND
TESTING

Fluids, Lubricants, and Elastomers Branch
Nonmetallic Materials Division

March 1980

TECHNICAL REPORT AFML-TR-79-4142

Final Report for Period September 1976 to March 1979

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This technical report has been reviewed and is approved for publication.

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) Fluoroalkyleneether silicate (FES) polymers (T_g 's -82°C to -91°C) were obtained from the reaction between fluoroether bis-dimethyl carbinols and bis-dimethyl-amino 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 commercial fluorocarbon elastomer (Viton GLT from DuPont), blends were prepared using the FES materials as an additive co-curing plasticizer. Temperature retraction tests demonstrated an optimum 9°F improvement in low temperature flexibility. O-ring seal evaluations in		

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Freon E6.5 fluid (chew and piston seal tests) demonstrated some seal enhancement and comparable durability in comparison to standard Viton GLT O-rings.

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FOREWORD

This report was prepared by the Fluids, Lubricants, and Elastomers Branch, Nonmetallic Materials Division. The work was initiated under Project No. 2421, Task No. 242101, Work Unit Directive 24210106, "Seals and Sealants". It was administered under the direction of the Air Force Materials Laboratory, Air Force Wright Aeronautical Laboratories, Air Force Systems Command, Wright-Patterson Air Force Base, Ohio with Captain Alan A. Shaffer as the AFML Project Scientist. Co-authors were Captain Alan A. Shaffer, Major Robert E. Cochoy, and Mr. William E. Berner, Air Force Materials Laboratory, (AFML/MBT).

This report covers research conducted from September 1976 to March 1979.

The authors wish to acknowledge the valuable technical contributions of Messrs. Thomas Wical and Wayne Polley (UDRI). Thanks is also extended to Dr. G. Ehlers (AFML/MBP) and Mr. E. Soloski (UDRI) for T_g and TGA analyses.

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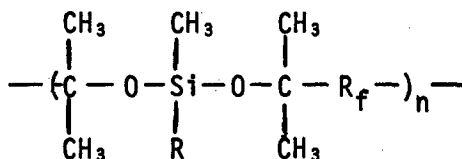
SECTION I

INTRODUCTION

The development of elastomeric materials providing improved serviceability for critical aircraft components such as hydraulic seals is an on-going goal of Air Force research. To date, 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 (registered tradename) by Dupont⁽¹⁾ this aspect of fluorocarbon elastomers was substantially improved.

In-house testing demonstrated static sealing capability of the Viton GLT as low as -46°C.⁽²⁾ In-house efforts focused on further improving the low temperature flexibility of the Viton GLT while maintaining all of its other excellent properties. It was felt this could be achieved by elastomer blending if the additive polymer could act as a co-curing reactive plasticizer.

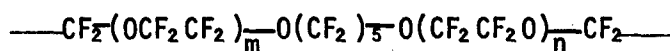
The additive polymer was a fluoroalkylene ether silicate with the following general structure:



R = methyl and/or vinyl

R_f = (CF₂OCF₂)_{6,7}, or 8

or

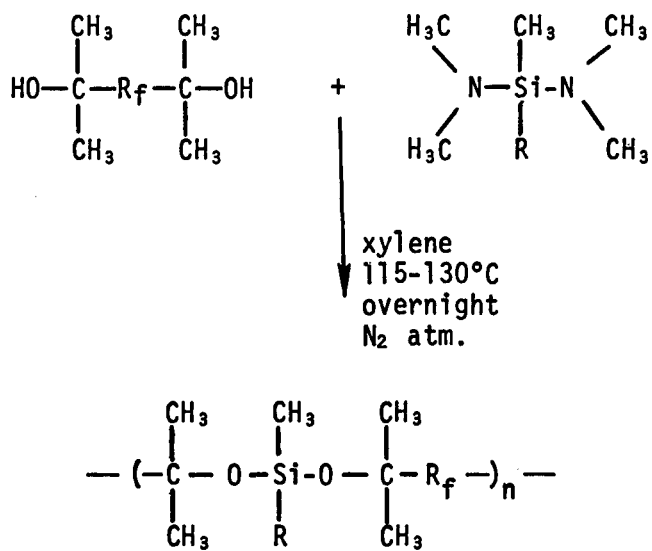


m + n = 5 or 6

This structure provided the chemical stability and low temperature flexibility of the fluoroether chain, peroxide cure reactivity at the pendant vinyl site, and hydrocarbon branching around the "hybrid silicate" bonding scheme to provide steric hindrance against hydrolysis.

This report describes a blending approach using this polymer in which the low temperature flexibility of the parent Viton GLT (as measured by TR-10) was improved with little or no sacrifice of any other physical property. This improved low temperature performance was verified by low temperature dynamic piston seal testing. The research involved both synthetic chemistry and elastomer blending and compounding studies.

The fluoroalkylene ether silicate polymers (designated FES in this report) were obtained by the condensation polymerization reaction between a bis-dimethyl carbinol containing the fluoroether segment and an appropriately substituted bis-dimethylamino silane derivative.⁽³⁾



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

Peroxide cure was obtained for the FES polymers using a variety of curing agents: Luperco 101XL, Varox, Di-Cup R, and Luperco CST. Only Luperco CST (the mildest curing agent listed above) gave optimum rubbery cures whereas all the others overcured the FES giving brittle vulcanizates. This embrittlement was reduced when lower vinyl content FES polymers were used. Luperco CST, however, did not cure Viton GLT at all, alluding to an inherent difference in the peroxide cure reactivities of the FES and Viton GLT components.

From the beginning and throughout the entire research effort, the optimum o-ring formulation for Viton GLT developed by DuPont served as a model and standard for comparison to the blends. TR-10 improvement with minimal sacrifice of any other physical property was the critical criterion of blend development. In the interest of minimal deviation from this standard (in hopes of maintaining overall physical properties), most blend formulations employed the same component loadings and cure cycles. The primary experimental variable was the relative quantities of Viton GLT and FES used. In all cases, their total was 100 pphr and their relative loadings will be abbreviated as pphr Viton GLT/pphr FES, i.e., 80/20, 70/30, 60/40, etc.

SECTION II

BLEND OPTIMIZATION

1. GROUP I (TABLE 2)

Initial blending studies were performed using FES polymers with one vinyl site in every repeating unit (2.3 to 2.7 mole % vinyl) and will be designated "high vinyl FES" throughout this report. Strong vulcanizate properties were obtained from a blend using an 80/20 ratio in the standard formulation, as shown by high tensile and hardness values. However, the ultimate elongation suffered presumably due to the high cure reactivity of the FES vinyl site. Use of more FES (as in the 60/40 ratio) only aggravated the problem, resulting in lowered elongation and strength.

On the other hand, use of a less reactive curing agent (Luperco CST) failed to cure the blend and was so weak that physical property measurements could not be taken. Reducing curing agent and co-agent quantities failed to give blends with satisfactory properties; elongations were well under 100% with very low tensile strengths.

It was evident at this point that the inherent difference in peroxide cure reactivities of the Viton GLT and FES components was preventing blend optimization. Conditions sufficient to adequately cure the Viton for required strength properties overcured the FES reducing prohibitively ultimate elongations. (TR-10 measurements are for the most part not reported at this stage because of their inaccuracies for elastomers having 100% or less ultimate elongation.) Conversely, use of less curing agent failed to give well co-cured blends, diluting the strength and elongation of the Viton GLT.

2. GROUP II (TABLE 2)

In an effort to prevent or reduce overcuring of the blends, FES polymers were synthesized having considerably lower vinyl concentrations (0.4 to 0.6 mole % vinyl), designated "low vinyl FES" throughout this report. Standard formulations using 80/20 ratios gave excellent elongations, adequate strengths, and somewhat improved TR-10's. 70/30 and 60/40 blends again displayed reduced strength and elongation, but not as greatly as with the high vinyl FES system. With a 90/10 blend, some TR-10 improvement was obtained with excellent maintenance of physical properties. Comparable results were achieved using the Varox curing agent. Again, use of lower co-agent concentrations (though improving elongation) greatly reduced strength and had no effect on TR-10.

3. GROUP III (TABLE 2)

To enhance the strength of the low vinyl FES blends, several runs employed higher filler and co-agent loadings. As expected, strengths improved greatly but at the prohibitive sacrifice of elongation. In one case, however, use of higher filler loadings for strength and lower curing co-agent loadings for elongation appeared to give some optimization with TR-10 improvement.

4. GROUP IV (TABLE 2)

Up to this point, the standard formulation with an 80/20 Viton GLT/low vinyl FES ratio appeared to give the best balance between strength, elongation, and improved TR-10. However, satisfactory blend performance had not yet been achieved since substantial TR-10 improvement had not yet occurred.

All blends so far prepared had used the Viton GLT standard press and post cure cycles. Several considerations led us to believe that the 500°F, 24 hour post cure cycle was too harsh for the FES system. Thermogravimetric analysis (in air at 20°C/min.) of the uncured FES polymers generally indicated very gradual weight loss below 300°C with rapid weight loss beginning above 300°C. However, in all cases, a slight weight loss was evident at 260°C (the 500°F post cure temperature). Over a 24 hour period, this weight loss presumably due to oxidative degradation could have been substantial, greatly reducing or completely destroying any plasticizing effect of the FES.

Several standard 80/20 blends were prepared with the low vinyl FES varying only the press and post cure cycles. One hour press cures at 260°F followed by 24 hour post cures at 260°F or 300°F were clearly inadequate as shown by the very low strengths and high elongations obtained. Extended post cures of another 24 hours at these temperatures produced worse results, possibly alluding to long term oxidative degradation of the uncured FES component.

However, several runs using the standard press cure and a 24 hour post cure at 350°F gave the best overall properties to date, with significantly improved TR-10. Strength properties were significantly lower than those for Viton GLT alone, but did reflect an adequately cured specimen for potential hydraulic o-ring seal application. These blends were quite obviously more loosely cured than earlier ones using the 500°F post cure. This was borne out by the significantly higher compression sets obtained for these blends.

5. GROUP V (TABLE 2)

Although the blends discussed above provided generally well-balanced properties with improved TR-10, they did present undesirable compromise

of Viton GLT's excellent strength and compression set resistance. From earlier work, it was evident that increased FES vinyl content gave stronger blends. Further, use of a lower post cure temperature appeared to enhance TR-10 improvement, presumably due to maintenance of the molecular weight and structural integrity (and thus plasticizing ability) of the FES component. A combination of these factors was hoped to provide optimization of the blend's strength (and hence compression set resistance) and low temperature flexibility (TR-10).

Several identical 80/20 blends using high vinyl FES were prepared again using standard component loadings. Standard press cures followed by 24 hour post cure cycles at 350°F, 400°F, and 500°F were performed to get a direct comparison of physical property behavior dependence on post cure temperature.

The 400°F post cure temperature gave superior overall results, the best yet achieved. Excellent TR-10 (-29.2°F) was obtained with high strength properties, significantly more than with the low vinyl FES. Elongation, though reduced somewhat, was still within acceptable limits. Another blend using another batch of high vinyl FES gave comparable results.

These latest blends were considered the optimum blends achieved in this research effort; significantly improved TR-10 values coupled with well-balanced satisfactory overall physical properties were achieved reproducibly. With the optimum blend finally obtained, several conclusions can be made in retrospect.

The relative degree of cure in the blend is controlled by the FES vinyl concentration; the greater the vinyl content the tighter the cure obtained. The post cure temperature of 500°F for 24 hours was too harsh for any FES polymer, causing oxidative degradation to the extent that

its plasticizing effect was nullified. Use of more moderate post cure temperatures (350°F or 400°F) and high vinyl FES gave optimization of physical properties, specifically maximally improved TR-10. The best ratio of Viton GLT to FES was 80/20 pphr. All other formulation variables were identical with those established by DuPont for Viton GLT o-ring seal application.

With the FES component comprising only 14% of the optimum blend formulation, it may be considered an additive polymeric system inducing markedly improved TR-10 while maintaining overall properties. The key to optimum blend performance was achieving the best combination of the FES co-curing and plasticizing roles. The highly reactive pendant vinyl groups regularly spaced in the FES backbone provided good co-curing with the Viton GLT at significantly lower post cure temperatures. The milder post cure conditions did not appear to degrade the FES inherent structure or molecular weight, allowing it to more effectively fullfill its plasticizing role.

TABLE 1

FES POLYMERS/STRUCTURE AND PROPERTIES

FES ^a #	STRUCTURE	T _g °C	TGA (in air 20°C/min)	ELEMENTAL ANALYSIS	MOLE % VINYL
1	$\begin{array}{c} \text{CH}_3 \\ \\ \text{---}(\text{O}-\text{C}-\text{CF}_2-\text{---}(\text{OCF}_2\text{CF}_2)_m-\text{O}-\text{CF}_2)_5-\text{O}-\text{CF}_2-\text{C}(\text{O}-\text{Si})_n-\text{---} \\ \\ \text{CH}_3 \end{array}$ $\begin{array}{c} \text{CH}_3 \text{ CH}_3 \\ \quad \\ \text{---}(\text{O}-\text{C}-\text{CF}_2)_m-\text{O}-\text{CF}_2-\text{C}(\text{O}-\text{Si})_n-\text{---} \\ \quad \\ \text{CH}_3 \text{ CH}_3 \end{array}$ $m + n = 5 \text{ or } 6$			C 27.28 H 1.29	2.35 (27.17) ^b (1.57)
2	$\begin{array}{c} \text{CH}_3 \text{ CH}_3 \\ \quad \\ \text{---}(\text{O}-\text{C}-\text{CF}_2\text{OCF}_2)_8-\text{C}(\text{O}-\text{Si})_n-\text{---} \\ \quad \\ \text{CH}_3 \text{ CH}_3 \end{array}$ $\begin{array}{c} \text{CH}_3 \text{ CH}_3 \\ \quad \\ \text{---}(\text{O}-\text{C}-\text{CF}_2\text{OCF}_2)_8-\text{C}(\text{O}-\text{Si})_n-\text{---} \\ \quad \\ \text{CH}_3 \text{ CH}_3 \end{array}$	-89	10% wt. loss at 290°C	C 27.12 H 1.64	2.42 (26.93) (1.62)
3	$\begin{array}{c} \text{CH}_3 \text{ CH}_3 \\ \quad \\ \text{---}(\text{O}-\text{C}-\text{CF}_2\text{OCF}_2)_7-\text{C}(\text{O}-\text{Si})_n-\text{---} \\ \quad \\ \text{CH}_3 \text{ CH}_3 \end{array}$ $\begin{array}{c} \text{CH}_3 \text{ CH}_3 \\ \quad \\ \text{---}(\text{O}-\text{C}-\text{CF}_2\text{OCF}_2)_7-\text{C}(\text{O}-\text{Si})_n-\text{---} \\ \quad \\ \text{CH}_3 \text{ CH}_3 \end{array}$	-82	Gradual wt. loss up to 295°C, then rapid wt. loss		2.70
4	$\begin{array}{c} \text{CH}_3 \text{ CH}_3 \\ \quad \\ \text{---}(\text{O}-\text{C}-\text{CF}_2\text{OCF}_2)_6-\text{C}(\text{O}-\text{Si})_n-\text{---} \\ \quad \\ \text{CH}_3 \text{ CH}_3 \end{array}$ $\begin{array}{c} \text{CH}_3 \text{ CH}_3 \\ \quad \\ \text{---}(\text{O}-\text{C}-\text{CF}_2\text{OCF}_2)_6-\text{C}(\text{O}-\text{Si})_n-\text{---} \\ \quad \\ \text{CH}_3 \text{ CH}_3 \end{array}$	-89	Start of slow wt. loss at 180°C, rapid loss at 360°C		0.44

^a Yields for all FES polymers ranged from 90 to 95%, inherent viscosities ranged from 0.10 to 0.15 dl/g in HFIP at 30°C.

^b Parenthetical values are theoretical.

TABLE 1 (Continued)

FES POLYMERS/STRUCTURE AND PROPERTIES

PES ^a #	STRUCTURE	T _g °C	TGA (in air 20°C/min)	ELEMENTAL ANALYSIS	MOLE % VINYL
5		-		C 27.73 H 1.89	(27.04) (1.82) 0.62
6		Initial wt. loss at 270°C; rapid wt. loss start at 330°C		C 26.50 H 1.63	(26.27) (1.63) 0.41
7	Same as #6 except copolymer ratio is 2.88 to 1	- 91	Initial wt. loss at 200°C; rapid wt. loss start at 310°C	C 27.12 H 1.80	(27.14) (1.67) 0.63
8	Same as #6 except copolymer ratio is 4.5 to 1			C 27.14 H 1.67	(26.49) (1.66) 0.44
9	Same as #4 except copolymer ratio is 7 to 1			C 27.87 H 2.05	(27.85) (2.06) 0.39

a yields for all FES polymers ranged from 90 to 95%, inherent viscosities ranged from 0.10 to 0.15 dl/g in HFIP at 30°C.

^b Parenthetical values are theoretical.

TABLE 2
BLENDING DATA SUMMARY

COMPONENTS (pph loadings)										PHYSICAL PROPERTIES			
FES (#) ^a	VITON	AUSTIN	MT	LUPERCO		OTHER	T _B , MPa (psi)	M ₁₀₀ , MPa (psi)	E _B , %	SHORE A HARDNESS	TR-10 ^b °C (°F)	COMP. SET COMMENTS	
	GLT	BLACK	BLACK	101XL	TAICA								
0 ^d	100	20	10	4	4	4	15.55 (2255)	8.76 (1270)	155	78	-29 (-20.2)	15%	
GROUP I													
20 (1)	80	20	10	4	4	4	14.97 (2170)		100	87		21.4%	
40 (2)	60	20	10	4	4	4	9.03 (1310)		80	86	-32 (-25.6)		
40 (2)	60	20	10	4	4	4	5.52 (800)		70	87			
40 (3)	60	20	10	4	4	4						Undercured	
20 (2)	80	20	10	4	4	2						Overcured	
20 (3)	80	20	10	4	4	2	5.81 (842)		100	92			
40 (3)	60	20	10	4	4	2	5.06 (733)		80	87			
40 (2)	60	20	10	4	4	2	8.38 (1215)		60	90			
40 (3)	60	20	10	4	4	2	3.03 (440)		70	87			
20 (3)	80	20	10	4	4	2	11.97 (1735)		100	90			

^a See Table 1.

^b 50% Elongation.

^c Compression sets performed on 214 size o-rings, 70 hours with 25% deflection at 204°C (400°F)

^d Standard Viton GLT o-ring formulation; standard press and post cure cycles used: 10 min. at 177°C, 4 hour rise to 260°C (500°F) plus 24 hours at 260°C, used on all blends unless otherwise noted.

^e Press cure: 30 min. at 166°C (330°F), post cure 24 hours at 204°C (400°F).

TABLE 2 (Continued)
BLENDING DATA SUMMARY

FES (#)			COMPONENTS (pph Loadings)					PHYSICAL PROPERTIES					
			VITON GLT	AUSTIN BLACK	MT BLACK	Ca(OH) ₂	TAICA	LUPERCO 101XL	OTHER	T _B , MPa (psi)	M ₁₀₀ , MPa (psi)	SHORE A HARDNESS	TR-10 °C (°F)
GROUP II													
20 (4)	80	20	10	4	4	4		9.55 (1385)	6.72 (975)	170	79	-31.7 (-25)	20.5%
20 (6)	80	20	10	4	4	4		9.95 (1443)		145	90	-30 (-22)	
20 (6)	80	20	10	4	4	4		12.04 (1746)	8.00 (1160)	160	84	-31 (-23.8)	
20 (7)	80	20	10	4	4	4		12.69 (1840)	8.90 (1290)	150	84	-32 (-25.6)	
30 (4)	70	20	10	4	4	4		7.69 (1115)	7.10 (1030)	107	82		
30 (5)	70	20	10	4	4	4		7.93 (1150)	6.93 (1005)	115	82		
40 (4)	60	20	10	4	4	4		5.38 (780)		105	85	-31.1 (-24)	
10 (6)	90	20	10	4	4	4		14.56 (2111)	10.11 (1466)	170	79	-30.8 (-23.5)	
20 (6)	80	20	10	4	4	4	4 Varox	11.08 (1607)		150	88		f
20 (6)	80	20	10	4	4	4	3.6 Varox	11.93 (1730)	9.81 (1423)	145		-30.5 (-22.9)	
20 (6)	80	20	10	2	2	4		11.55 (1675)	2.87 (417)	200	78	-30.5 (-22.9)	

f Press cure: 15 min. at 177°C, post cure: same as with Luperco 101XL.

TABLE 2 (Continued)

BLENDING DATA SUMMARY

FES (#)	COMPONENTS (pph loadings)					PHYSICAL PROPERTIES							
	VITON GLT	AUSTIN BLACK	MT BLACK	Ca(OH) ₂	TAICA	LUPERCO 101XL	OTHER	T _B , MPa (psi)	M ₁₀₀ , MPa (psi)	EB, %	SHORE A HARDNESS	TR-10 °C (°F)	COMP. SET COMMENTS
GROUP III													
20 (6)	80	32	16	6.4	6.4	4		13.09 (1898)		90	85		
40 (6)	60	32	16	6.4	6.4	4		8.16 (1183)		72	86		
20 (6)	80	32	16	6.4	6.4	6.4		17.15 (2487)		75	90		
20 (6)	80	32	16	6.4	6.4		6.4 Varox	14.25 (2066)		110	88		
20 (6)	80	32	16	6.4	6.4		5.8 Varox	14.76 (2140)		85	90		
20 (6)	80	32	16	2	2	4		11.38 (1644)	9.34 (1355)	135	88	-31.5 (-24.7)	

TABLE 2 (Continued)
BLENDING DATA SUMMARY

COMPONENTS (pph loadings)				PHYSICAL PROPERTIES						COMP. SET			
FES (#)	VITON GLT	AUSTIN BLACK	MT BLACK	Ca(OH) ₂	TAICA	LUPERCO 101XL	T _B , MPa		M ₁₀₀ , MPa		SHORE A HARDNESS	TR-10 °C (°F)	COMMENTS
							(psi)	(psi)	(psi)	(psi)			
GROUP IV													
20 (5)	80	20	10	4	4	4	3.59 (520)	3.31 (480)	2.76 (400)	2.31 (336)	610 500	-30.5 (-22.9)	g
20 (5)	80	20	10	4	4	4	3.79 (549)	3.47 (503)	2.63 (381)	2.10 (305)	550 450	-30.5 (-22.9)	h
20 (7)	80	20	10	4	4	4	11.79 (1710)		7.33 (1063)		160	-32.7 (-26.8)	i
20 (5)	80	20	10	4	4	4	10.19 (1478)		8.71 (1263)		160	-32.0 (-25.6)	j
20 (8)	80	20	10	4	4	4	8.00 (1160)		5.52 (800)		155	-32.28 (-26.1)	32% ^{k*}
20 (9)	80	20	10	4	4	4	7.66 (1110)		6.24 (905)		145	-32.7 (-26.9)	35% ^{k*}

g Press cure: 60 minutes at 127°C (260°F)

Post cure: 24 hours at 127°C (260°F)

Values to right obtained after 48 hour post cure at 127°C.

h Press Cure: 60 minutes at 127°C

Post Cure: 24 hours at 149°C (300°F)

Values to right obtained after 48 hour post cure at 149°C.

i Press Cure: 10 minutes at 177°C (350°F)

Post Cure: 24 hours at 177°C in air

j Press Cure: 10 minutes at 177°C

Post Cure: 24 hours at 177°C in nitrogen

k Large scale formulations (see experimental section); standard press cure with 24 hour post cure at 177°C in air.

*O-ring evaluation studies performed
Compounds I and II, respectively.

TABLE 2 (Continued)

BLENDING DATA SUMMARY

FES (#)			COMPONENTS (pph loadings)						PHYSICAL PROPERTIES					
			VITON GLT	AUSTIN BLACK	MT BLACK	Ca(OH) ₂	TAICA	LUPERCO 101XL	OTHER	T _B , MPa (psi)	M ₁₀₀ , MPa (psi)	ER, %	SHORE A HARDNESS	TR-10 °C (°F)
GROUP V ^L														
20 (2)	80	20	10	4	4	4	4	4	10.17 (1475)	8.55 (1240)	135	82	-34.3 (-29.7)	m
20 (2)	80	20	10	4	4	4	4	4	9.24 (1340)	7.28 (1055)	140	83	-33.5 (-28.3)	n
20 (2)	80	20	10	4	4	4	4	4	10.48 (1520)	9.66 (1400)	130	85	-34.0 (-29.2)	o
20 (2)	80	20	10	4	4	4	4	4	9.69 (1405)	6.93 (1005)	150	84	-32.3 (-26.1)	p
20 (3)	80	20	10	4	4	4	4	4	11.52 (1670)	10.62 (1540)	120	84	-33.8 (-28.8)	q
20 (r)	80	20	10	4	4	4	4	4	11.45 (1660)	10.24 (1485)	125	83	-34.0 (-29.2)	16.1*

^L All runs in this group used the standard press cure.

^m Post cure: 24 hours at 177°C (350°F)

ⁿ Post cure: 24 hours at 177°C (350°F)

^o Post cure: 24 hours at 204°C (400°F)

^p Post cure: 24 hours at 260°C (500°F)

^q Post cure: 24 hours at 204°C (400°F)

^r Large scale formulation using blend of FES 1, 2, and 3. See experimental section. Post cure: 24 hours at 204°C.

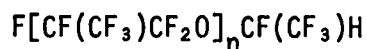
*0-ring evaluation studies performed
Compound III

SECTION III

O-RING EVALUATION

To determine if this improvement in TR-10 could be manifested in a practical hydraulic seal application, three 44 gram scale formulations were prepared each from which 18 standard 214 size o-rings were fabricated. The first two sets of o-rings were prepared from low vinyl FES and designated Compounds I and II (see blend data summary chart, Group IV). The last o-ring batch (Compound III) was prepared from a mixture of three high vinyl FES polymers (see blend data summary chart, Group V). Direct performance comparison could then be made between o-rings containing low and high vinyl FES materials.

Due to the limited number of o-rings available, a single hydraulic test fluid had to be chosen. Air Force research objectives in hydraulic system performance (the development of a nonflammable fluid and compatible seal material to improve survivability and safety) became important in this selection. Of the two candidate fluids being considered by the Air Force (Halocarbon A0-8 produced by Halocarbon Products Corporation and Freon E-6.5 produced by DuPont), Viton GLT had demonstrated good compatibility in the latter fluid. Freon E-6.5, having the structure



$$n = 5,6$$

was therefore selected as the test fluid of choice for performance evaluation of the FES blend o-rings.

Before extended o-ring seal testing was begun, several initial screening tests were performed; hydrolytic aging studies to verify the stability of the silicate bonding scheme in this regard and compatibility tests in the Freon E-6.5 fluid. Identical tests were performed on standard Viton GLT o-rings to obtain baseline data for comparison.

Hydrolytic aging tests (Table 3) indicated good stability of the FES blend o-rings, comparing very favorably with the base Viton GLT compound. Compatibility was also evident from the Freon E-6.5 aging studies (Table 4). One important difference was noted from the Freon aging tests; Compound II (low vinyl FES) had greater swell than the more tightly cured Compound III (high vinyl FES). A certain degree of swell is generally considered favorable for o-ring sealing performance in that it helps to compensate for any compression set taken by the o-ring during service. Although Compound I was not initially checked in the Freon fluid (due to a shortage of o-rings), it could be expected, due to its similarity of composition to Compound II, to exhibit comparable swell. This may have been an important factor in the improved low temperature sealing evident with Compound I discussed in the next section.

With initial screening tests accomplished, indicating good hydrolytic stability and Freon E-6.5 compatibility, the research effort focused on obtaining detailed low and high temperature sealability data for both the FES blend and standard Viton GLT o-rings.

TABLE 3

PERCENT WEIGHT CHANGE (CUMULATIVE TOTALS) AND PHYSICAL PROPERTIES
OF VITON GLT AND FES BLEND O-RINGS RESULTING FROM HYDROLYTIC AGING (95% R.H. AT 93°C (200°F) EXPOSURE)

TIME (hours)	PERCENT WEIGHT CHANGE COMPOUNDS					PHYSICAL PROPERTIES*							
	VITON GLT		I	II		VITON GLT		I		II			
	Orig	Aged	Orig	Aged		Orig	Aged	Orig	Aged	Orig	Aged		
24	-	+0.74	+0.59	+0.68	Tensile Strength, psi	1806	710	725	860	660	680	1420	1087
48	-	+0.74	+0.60	-	Elongation, %	155	87	100	115	90	100	106	120
72	+1.37	+0.75	+0.62	+0.71	Hardness, Shore A, pts. 82-84	79	78	79	78	78	80	83	82
168	+1.19	+0.95	+0.65	+0.86	100% Modulus, psi	1226	-	725	805	-	675	-	-
336	+1.34	+1.28	+0.93	+0.87	*Viton GLT and Compound III exposed for 672 hours, Compounds I and II exposed 504 hours.								
504	-	+1.38	+0.99	-									
672	+1.42	-	-	+1.00									

TABLE 4
 PHYSICAL PROPERTIES OF VITON GLT AND FES BLEND O-RINGS
 AFTER AGING IN FREON E-6.5 FLUID 70 HOURS AT 135°C (275°F)

PROPERTY	COMPOUNDS			ORIGINAL		
	VITON GLT	II	III	VITON GLT	II	III
Tensile Strength, psi	2055	854	1324	1806	660	1420
Elongation, %	150	118	107	155	87	106
Hardness, Shore A	76	78	78	82-84	78	83
100% Modulus, psi	1140	786	1240	1226	-	-
Volume Change, %	+2.31	+8.91	+4.44			
Fluid Condition	Clear/ Colorless	Clear/ Colorless	Clear/ Colorless			

The initial seal formulations were screened for "basic cycling behavior" in a test device called a "chew tester" which is shown in Figure 1. The chew test has built-in dynamic cycling performance requirements that serve to screen candidate seal materials. The test was conducted for a specific number of cycles rather than to complete failure of the seal. Seal material performance was based on a leakage criteria and a post-test examination of the seals. The test conditions were:

Temperature	- 135°C (275°F)
Pressure (cyclic)	- 20.68 MPa (3,000 psig)
Stroke Length	- 7.5 cm (3.0 inches)
No. of Cycles	- 100,000
Back-up Rings	- MS-27595 (Teflon)

A piston seal test device was used to determine low temperature seal performance. The specific test procedure used in this program was designed not only to determine low temperature sealability but also the ability of the seal to reseal at low temperature following several high temperature excursions.

A flow chart is shown in Figure 2 that describes the types of tests conducted to determine low temperature sealability and resealability. Each seal was initially checked for low temperature leakage at -54°C (-65°F). If the seal leaked, the temperature was raised 5.6°C (10°F) and again checked for sealability. This process continued until the lowest temperature was determined at which a non-leaking 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 inch stroke, 30 cycles/minute. Approximately 10,000 cycles were conducted during this phase and seal leakage was recorded. Following the high temperature cycling, the temperature was

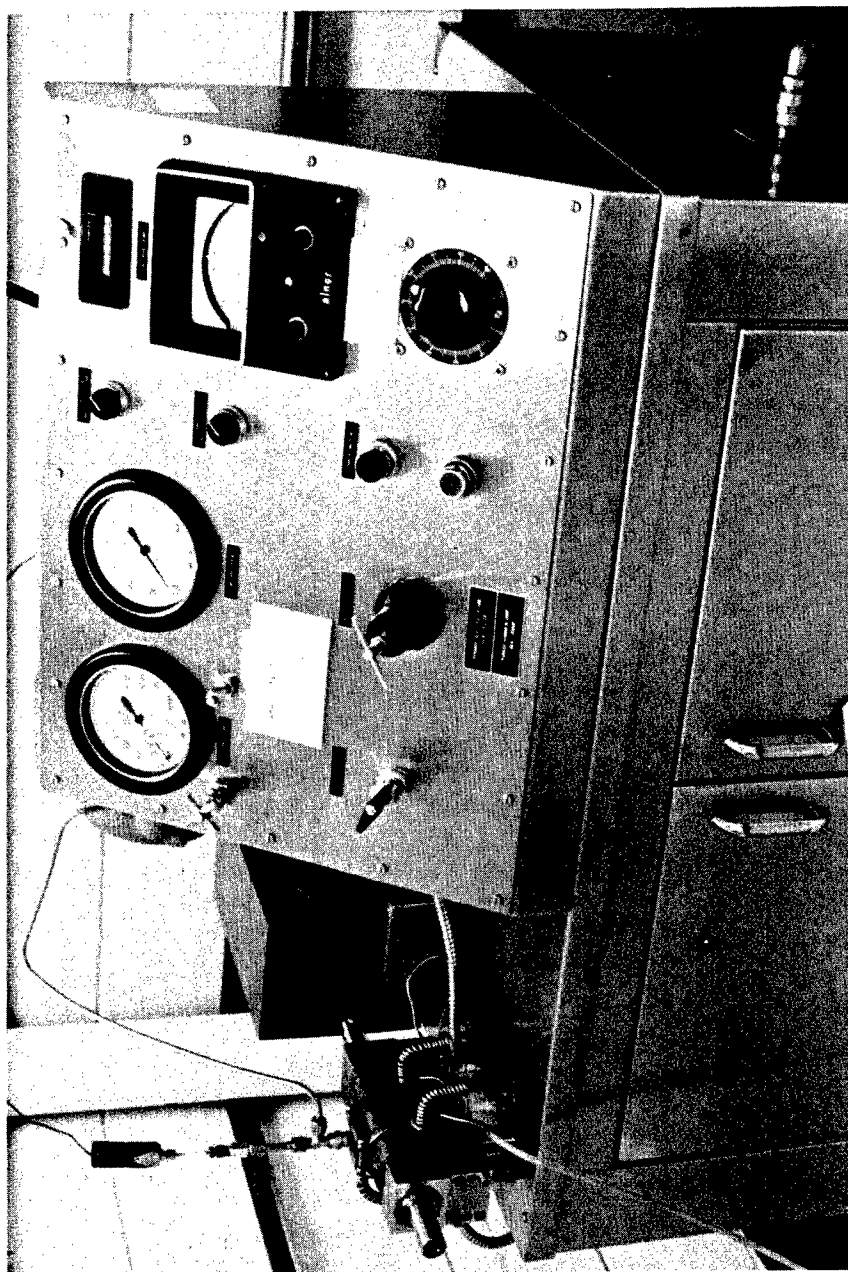


Figure 1. Photograph of Chew Test Apparatus

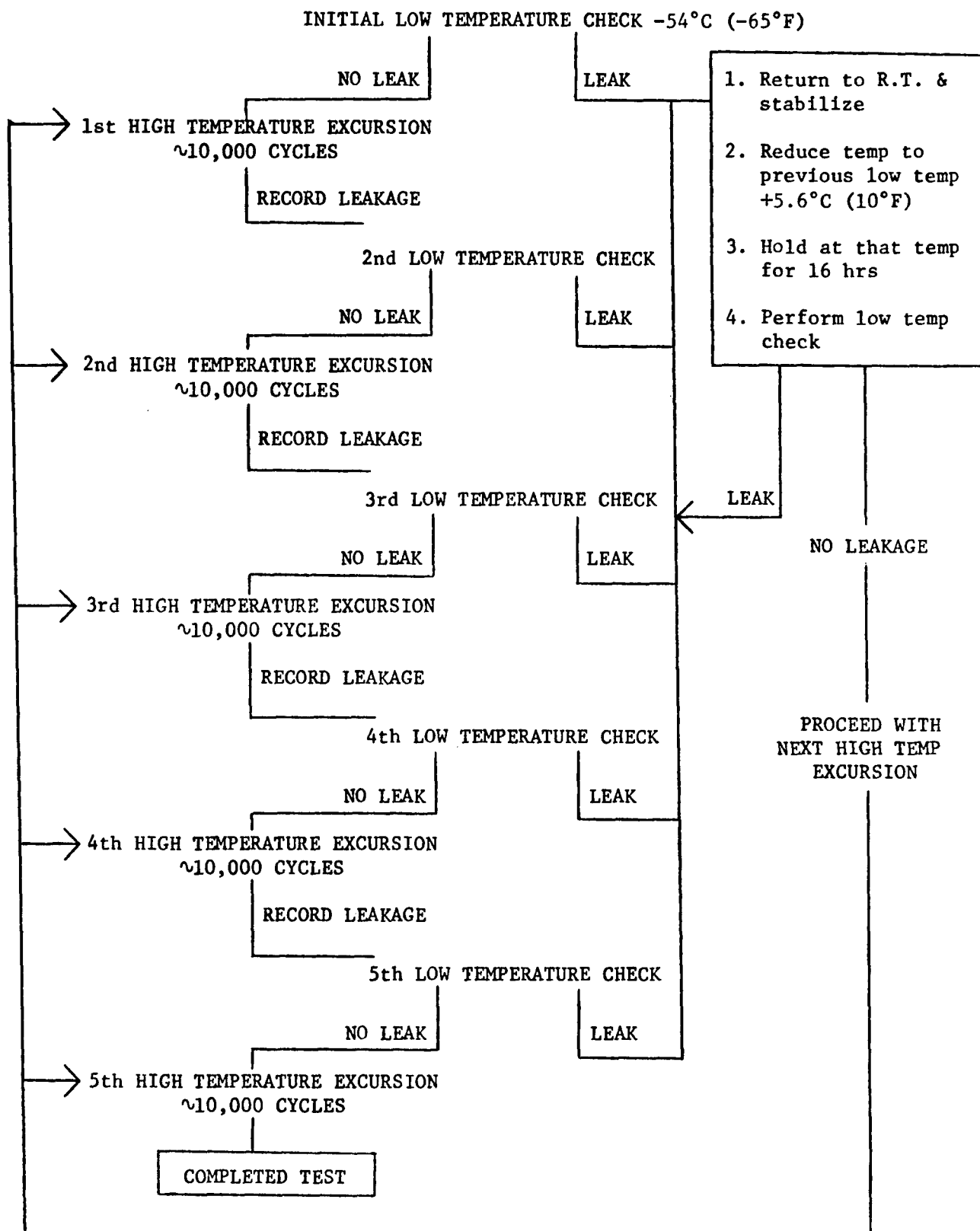


Figure 2. Flow Chart for Piston Seal Tests

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. A photograph of the piston seal test apparatus is shown in Figure 3.

1. DYNAMIC CYCLING TEST RESULTS

a. Chew Tests. Baseline data for the chew and piston seal tests were obtained using the Viton GLT o-ring compound in the Freon E-6.5 nonflammable hydraulic fluid. Chew test results showed the seals to be only slightly worn and the total leakage recorded for the four seals tested ranged from 0.3 to 1.2 ml. A total leakage of over 20 ml would be considered as questionable seal performance and a leakage of over 30 ml would be considered as failure. No compression set or nibbling was evident. The results of these tests are shown in Table 5.

Two FES blends were evaluated against the Viton GLT baseline. Compound II performed well in the chew test indicating only slight leakage over the 100,000 cycles. The post-test evaluation of the rings showed them to be in excellent condition. One of the test cells (including two test seals) failed early because of an imperfection in one of the seals. These seals were known to contain flaws prior to the initiation of these tests but only limited quantities of the seal material were available so all seals were tested.

Compound III performed as well as did the previous blend. The post-test evaluation of the seals showed two of the seals to be slightly worn and the other two to be in excellent condition. Leakage levels for both the FES blends were very low for this test.

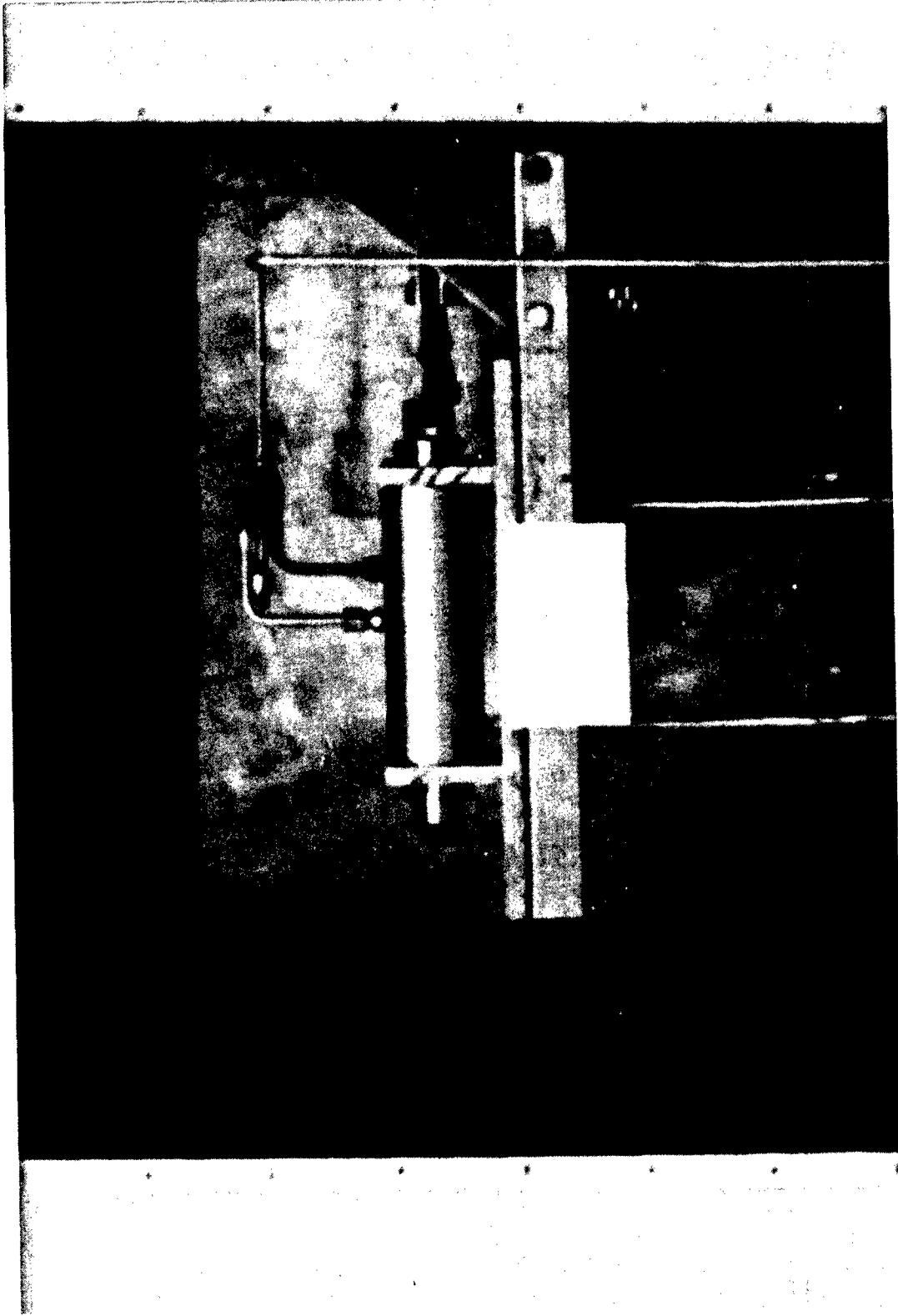


Figure 3. Photograph of Piston Seal Test Apparatus

TABLE 5
CHEW TEST RESULTS

<u>MATERIAL</u>	<u>FLUID</u>	<u>CYCLES</u>	<u>LEAKAGE (ml)</u>	<u>SEAL CONDITION</u>
Baseline				
Viton GLT	Freon E-6.5	100,000	1.2	Excellent
Viton GLT	Freon E-6.5	100,000	0.3	Excellent
Viton GLT	Freon E-6.5	100,000	1.0	Excellent
Viton GLT	Freon E-6.5	100,000	0.5	Excellent
FES Blends				
Compound II	Freon E-6.5	100,000	0.5	Excellent
Compound II	Freon E-6.5	100,000	2.0	Excellent
Compound III	Freon E-6.5	100,000	2.0	Slight Wear
Compound III	Freon E-6.5	100,000	1.4	Slight Wear
Compound III	Freon E-6.5	100,000	1.6	Excellent
Compound III	Freon E-6.5	100,000	1.2	Excellent
Compound III	MIL-H-5606	583	50	Destroyed
Compound III	MIL-H-5606	583	50	Destroyed
Compound III	MIL-H-5606	583	50	Destroyed
Compound III	MIL-H-5606	583	50	Destroyed

b. Piston Seal Test Results. The Viton GLT piston seal test results in the Freon E-6.5 fluid showed that a seal was initially established at -34.4°C (-30°F). Low temperature sealability following the five high temperature excursions was also maintained at -34.4°C . High temperature cyclic leakage was minimal after 50,000 cycles. In an effort to estimate the durability of the seals, the high temperature excursions were continued for an additional 150,000 cycles at 135°C . This cycling was performed at a cycling rate of 30 cycles/minute for approximately 6 hours/day and took approximately four weeks to complete. The seals were at room temperature for the remainder of the day and also on weekends. The total leakage for the Viton GLT seals ranged from 0.7 ml to 7.9 ml for the four seals tested. These are very low leakage levels, particularly for a piston seal, considering the length of the test and the number of cycles conducted. A post-test examination of the seals showed them to be in excellent condition. Test data for the Viton GLT and FES blends evaluated in the piston seal test apparatus are summarized in Table 6.

Compound II FES seals were selected for the piston seal test. The initial low temperature seal for Compound II was -34.4°C . No leakage was recorded at that temperature. The temperature was lowered to -37.2°C (-35°F) but a slight leak was observed on one of the test seals. Following the low temperature checks, the seals were cycled according to the schedule in Figure 2. After 24,280 cycles, the left of test cell #1 started leaking severely and that test cell was removed from the test. Leakage up to that point for both seals was almost zero. A post-test examination of the two test rings showed that the seal that failed was split and chewed in the area of the mold parting line. Its mating seal in the same test cell was only slightly worn (as if the surface was dull) but was otherwise in excellent condition. The premature failure of the left ring was probably due to an imperfection in the ring and not the result of material degradation. The seal specimens for these tests were prepared from a very limited supply of FES polymer. Only a few seals could be molded from this limited supply. Some of the seals used for these tests were not in perfect condition but were the best available.

TABLE 6
PISTON SEAL EVALUATIONS OF FES BLEND O-RINGS

MATERIAL	FLUID	TEST CELL	POSITION	LOWEST SEAL TEMP °C (°F)	LOWEST RESEALABILITY TEMP °C (°F)	TOTAL LEAKAGE AFTER () CYCLES		SEAL CONDITION
						50,000 (ml)	200,000 (ml)	
Compound I	Freon E-6.5	1	Left	-37.2 (-35)	-37.2 (-35)	0.3	-	Very Good/ Slight Abrasion
Compound I	Freon E-6.5	1	Right	-37.2 (-35)	-37.2 (-35)	1.2	-	Very Good/ Slight Abrasion
Compound I	Freon E-6.5	3	Left	-37.2 (-35)	-37.2 (-35)	0.2	-	Very Good/ Slight Abrasion
Compound I	Freon E-6.5	3	Right	-37.2 (-35)	-37.2 (-35)	1.5	-	Very Good/ Slight Abrasion
Compound II	Freon E-6.5	1	Left	-34.4 (-30)	-34.4 (-30)	Severe	-	Poor/Split
Compound II	Freon E-6.5	1	Right	-34.4 (-30)	-34.4 (-30)	0	-	Excellent
Compound II	Freon E-6.5	3	Left	-34.4 (-30)	-34.4 (-30)	0	0.2	Very Good/Nicked
Compound II	Freon E-6.5	3	Right	-34.4 (-30)	-34.4 (-30)	0	0.4	Excellent
Compound III	Freon E-6.5	1	Left	-34.4 (-30)	-34.4 (-30)	0.3	-	Excellent
Compound III	Freon E-6.5	1	Right	-34.4 (-30)	-34.4 (-30)	0.8	-	Excellent
Compound III	Freon E-6.5	3	Left	-34.4 (-30)	-34.4 (-30)	0.1	-	Excellent
Compound III	Freon E-6.5	3	Right	-34.4 (-30)	-34.4 (-30)	0.1	-	Excellent

TABLE 6 (Continued)

PISTON SEAL EVALUATIONS OF FES BLEND O-RINGS

MATERIAL	FLUID	TEST CELL	POSITION	LOWEST SEAL TEMP	LOWEST RESEALABILITY	TOTAL LEAKAGE AFTER () CYCLES		SEAL CONDITION
				°C (°F)	TEMP °C (°F)	50,000 (ml)	200,000 (ml)	
Viton GLT	Freon E-6.5	1	Left	-34.4 (-30)	-34.4 (-30)	0.7	-	Excellent
Viton GLT	Freon E-6.5	1	Right	-34.4 (-30)	-34.4 (-30)	0.8	-	Excellent
Viton GLT	Freon E-6.5	3	Left	-34.4 (-30)	-34.4 (-30)	2.1	-	Excellent
Viton GLT	Freon E-6.5	3	Right	-34.4 (-30)	-34.4 (-30)	7.9	-	Excellent
Compound III	MIL-H-5606	1	Left	These seals would not				Destroyed
Compound III	MIL-H-5606	1	Right	maintain				Destroyed
Compound III	MIL-H-5606	3	Left	a seal at any				Destroyed
Compound III	MIL-H-5606	3	Right	temperature.				Destroyed

The two Compound II seals in test cell #3 continued until the end of the 50,000 cycle phase of the test and no leakage was recorded during that cycling period. Testing with cell #3 was continued as was the Viton GLT until reaching a maximum of 200,000 cycles. The total leakage at that time was less than 1 ml per seal. Total leakage recorded was 0.2 ml for the left seal and 0.4 ml for the right seal. A post-test examination of the seals showed that the left seal had a rather large nick in it but was otherwise in excellent condition. Again, this appeared to be a flaw-related failure rather than an inherent materials problem. The right seal was in excellent condition with the only wear showing as a dulled surface finish.

The FES blend Compound I was also evaluated in the piston seal tester. This blend maintained a low temperature seal at -37.2°C (-35°F) with no leakage recorded. The seals were then cycled at 135°C according to the procedures shown in Figure 2. After each high temperature excursion, the Compound I blend resealed at -37.2°C with no leakage recorded. The total accumulated leakage over the 50,000 cycle high temperature test was very small (approximately 1 ml per seal). The post-test evaluation of the seals showed that all of the rings were abraded slightly. The degree of abrasion was slightly more severe in 50,000 cycles than was observed with the Compound II blend after 200,000 cycles. Because of the limited amount of time available for testing, the Compound I blend was not evaluated over the 200,000 cycle period.

The third FES blend, Compound III, was evaluated in the piston seal tester and also maintained a seal at -34.4°C . After high temperature cycling excursion, it resealed at -34.4°C . The high temperature leakage data recorded for the Compound III seals were almost zero for all seals. None of the seals leaked over 1 ml during the 50,000 cycle test. A post-test evaluation of the seals showed them to be in near perfect condition. Unfortunately, time did not permit the long term durability testing of this formulation.

2. PISTON SEAL TEST RESULTS IN MIL-H-5606C HYDRAULIC FLUID

For comparison, tests were performed in the currently used hydrocarbon based Air Force hydraulic fluid MIL-H-5606C. Tests of Compound III were initiated simultaneously in the chew tester and piston seal tester. In the chew tester, Compound III cycled for only 585 cycles before extremely high leakages were recorded. The post-test evaluation of the seals showed that they were nearly completely destroyed with only a fraction of the seals remaining. Failure was caused by nibbling. The Compound III seals tested in the piston seal tester at the same time would not maintain a seal at any temperature. An examination of these seals showed that the o-ring deteriorated severely even without cycling.

Although not previously tested for compatibility with MIL-H-5606, this type of total seal failure was unexpected. Later tests showed that these seals were not compatible with MIL-H-5606 fluid. These results were summarized in Table 6.

3. SUMMARY

The FES Compound I showed a 2.8°C (5°F) improvement in sealability at low temperatures over the Viton GLT. No seal leakage was recorded after exposure to the -37.2°C (-35°F) environment for 16 hours. After each high temperature excursion, it also resealed at -37.2°C. Only minor leakages were recorded during the high temperature cycling.

The FES Compounds II and III sealed equally as well at low temperatures as did the Viton GLT. No leakage was recorded after the exposure to -34.4°C (-30°F) for 16 hours. The resealability temperature was also found to be -34.4°C. The durability of the seal, based on the results of the long term piston seal tests, appeared to be excellent. Lower leakage levels for the Compound II and III FES blends were observed than were recorded with the Viton GLT.

SECTION IV

CONCLUSIONS

Improved low temperature flexibility of the Viton GLT/FES blends was reflected by TR-10 measurements. O-ring sealing tests indicated performance at least comparable to Viton GLT with some low temperature sealing enhancement (Compound I). However, it is possible that this improved sealing was due to a number of factors in addition to TR-10, particularly swell. Of equal significance are the lower leakage rates obtained for the FES o-rings over Viton GLT, indicating that the plasticizing effect may have also aided sealing capability at high temperatures (135°C).

Certain limitations existed throughout this research effort; the most important of which was the low molecular weight of the FES materials. Significantly higher molecular weight FES (inherent viscosity .3 to .5 dl/g) could have better dispersion/plasticizing capabilities. More co-curing with the Viton GLT would result giving, in turn, greater strength properties.

Results along these lines were obtained early in the research effort from a standard 80/20 Viton GLT/gelled high vinyl FES (#2) blend.

TABLE 7
 PHYSICAL PROPERTIES¹ OF GELLED FES BLEND IN COMPARISON

	<u>T_B,MPa</u> <u>(psi)</u>	<u>M₁₀₀,MPa</u> <u>(psi)</u>	<u>E_B,%</u>	<u>SHORE A</u> <u>HARDNESS</u>	<u>TR-10 °C</u> <u>(°F)</u>
Gelled FES #2 ²	15.03 (2180)	14.0 (2030)	130	84	-32.8 (-27)
Viton GLT	15.55 (2255)	8.76 (1270)	155	78	-29 (20.2)
Group V ³	10.57 (1533)	9.27 (1344)	130	83.4	-33.9 (-29)
Group IV ⁴	9.41 (1364)	6.95 (1007)	155	78	-32.4 (-26.4)

¹ Standard press cure used throughout: 10 min. at 177°C.

² Post cures for gelled FES and Viton GLT 24 hours at 260°C.

³ Average of runs using 177°C and 204°C post cures.

⁴ Average of runs using 177°C.

Remarkable data evident here were the very high tensile and, particularly, modulus values compared to average values from Group IV blends, Group V blends, and the Viton GLT compound alone. Comparison of the modulus data in particular (known to be linearly dependent on cross link density) indicates a crosslink density of much greater magnitude than in any ungelled FES blend or even the Viton GLT standard compound. Crosslink density also increases in going from low to high vinyl FES blends at which point it appears to be comparable to that of Viton GLT alone.

The trends evident in the modulus data in Table 7 can give insight to the FES/Viton GLT interaction at bulk molecular level. The low vinyl FES blends (Group IV) indicate an adequate degree of co-curing (cross-linking between Viton GLT and FES) to provide sufficient strength and TR-10 improvement. However, they have an overall diluent effect on the Viton GLT, lowering its crosslink density in relation to the standard Viton GLT compound. This is consistent with the goal of that phase of blend development; to achieve a more loosely cured blend (in relation to the standard) by using a low mole percent concentration of vinyl cure sites.

The high vinyl FES blends (Group V) reflect a crosslink density comparable or slightly greater than Viton GLT. The diluent effect (based on modulus) is not present here. Co-curing evidently went further in these blends giving greater strength and, because of increased FES/Viton GLT interaction, improved TR-10. These results are qualitatively consistent with the much higher vinyl cure site concentrations used.

For the gelled high vinyl FES material, these interaction processes obviously 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 weights of the ungelled FES materials (0.10 to 0.15 dl/g inherent viscosity). This gelled FES material (taffy-like consistency), in spite of its crosslinked state, could still have dispersed thoroughly in the main body of Viton GLT polymer. (On the mill, heat build-up could have broken down crosslink density, aiding dispersion.) In any event, the higher molecular weight FES could provide more entanglement with the Viton GLT giving a more homogeneous system with closer and greater amount of proximity of FES and Viton GLT polymer chains. This greater proximity, in turn, would increase co-curing between these systems giving higher crosslink density and much higher strength. Along with this co-curing intimacy would be an effective reduction of the tendency of Viton GLT to crystallize at low temperatures, giving the improved TR-10.

These gelled FES data were not presented earlier because of their anomalous nature and the fact that FES gelation could not be reproduced, precluding reproduction of the data. However, these data may allude to what can be done with higher molecular weight ungelled FES polymers obtained in reproducible fashion. Unfortunately, time restrictions precluded an intense synthesis effort aimed at obtaining higher molecular weight FES polymers. Several approaches do exist for future investigation in this regard, including use of freon co-solvents, variation of silane monomer leaving groups (acetoxo, N-methylacetamido, ureido), and use of condensation polymerization catalysts.

In final summary, the basic approach of using low Tg fluoroalkylene ether copolymers (FES) as plasticizers for fluorocarbon elastomers (Viton GLT) to improve TR-10 performance has been verified. Minimal sacrifice (and, in some cases, enhancement) of strength properties came about because of co-curing of the fluoroether plasticizer with the base Viton GLT polymer.

Maximum TR-10 improvement reproducibly obtained was 9°F. This perhaps was not of great enough magnitude to be reflected reproducibly in low temperature o-ring seal testing. However, the o-ring testing did demonstrate (based on chew and piston seal tests in Freon E-6.5 fluid) that the durability and overall seal capabilities of the FES blend o-rings were comparable or slightly improved over Viton GLT. This indicated the permanence of the co-cured FES plasticizer, not leaching out of the system; a common problem with standard plasticizer materials.

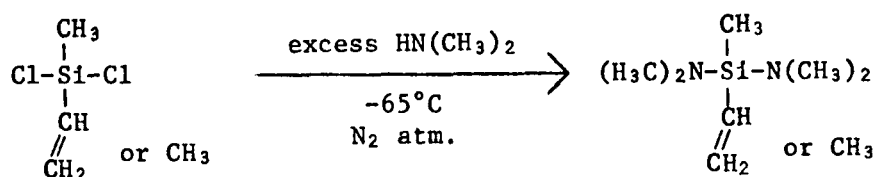
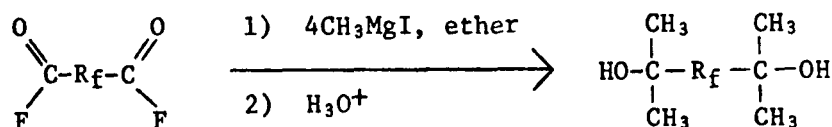
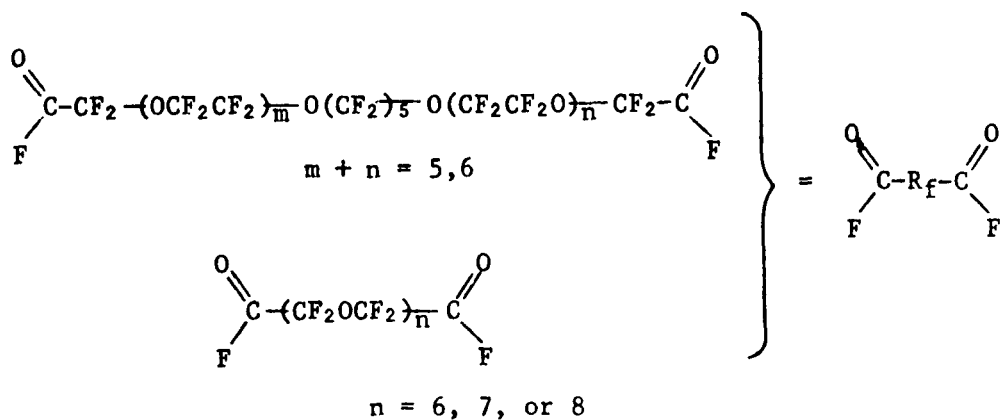
Future improvements on this basic blending approach to fluorocarbon elastomer development (including use of higher molecular weight additive materials containing longer fluoroether chains) can perhaps increase the magnitude of low temperature flexibility obtained. A more difficult problem to approach is providing a greater degree of cure control; to provide, in effect, equivalent peroxide reactivity (cure rates) to the Viton and FES systems. This would provide a magnitude of co-curing previously unattained and could make a dramatic difference in resultant physical properties. Altering curing/co-agent materials or concentrations was unsuccessful in this regard. Synthesis of new FES polymers with varying peroxide curable pendant groups (i.e. oxymethyl) is an alternative approach. It should be emphasized as a final note that the potential of this blend approach is by no means limited to the FES system. Any low Tg polymer compatible with fluorocarbon elastomers might be successfully used, provided it could take part in the curing process.

SECTION V

EXPERIMENTAL

1. SYNTHESIS

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



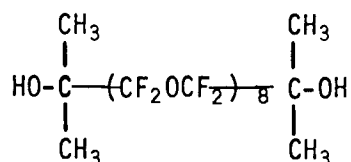
The ether di-acid fluorides (EDAF's) and dichlorosilanes were prepared and supplied by PCR, Inc., Gainesville, FL.⁽⁴⁾

The general experimental procedure for preparation of the fluoroether bis-dimethyl 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 1.65g (70 g-atoms) of Mg turnings. Anhydrous ethyl ether (40 ml) was added to the flask and, under a dry nitrogen blanket, 9.0g (63 mmoles) 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 minutes. Then 20 ml of dry F-2-butylfuran was added all at once to the Grignard solution. A solution of an EDAF (10 mmoles) 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 (approx. 5 drops per second) was satisfactory. After addition of the EDAF solution, the reaction mixture was heated to reflux for one hour. 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 (approx. 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 X 50 ml), saturated $NaHCO_3$ (1 X 50 ml), and H_2O (1 X 50 ml) and dried over $MgSO_4$.

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



had a b.p. 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%. $\text{C}_{22}\text{H}_{14}\text{F}_{32}\text{O}_{10}$ 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 inch magnetic stir bar, and nitrogen gas inlet was added methyl vinyl dichlorosilane (or dimethyl dichloro silane) (0.105 moles) along with 200 ml of dry petroleum ether (b.p. range 30-50°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 (25.0g, 0.5 moles) 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, 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" Vigreux column under nitrogen atmosphere. The products were

obtained at 143-145°C and 125-128°C b.p., 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:

The bis dimethylcarbinol (6.7 mmoles) was added to a 50 ml, three-necked, round-bottom flask equipped with a 1 inch 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. 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 mmoles, 4.2g) 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 hours. 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 (0.1mm 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 mmoles) and bis (dimethylamino) methyl vinyl silane (9.0 mmoles) was added to the diol solution. Also, the 23 hour reaction temperature used was 115°C. Mole percent 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, Tg, TGA, and elemental analyses for the FES polymers are presented in Table 1.

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).

2. 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 again take on 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" x 1" and 3" x 1-1/8") using the following component loadings for the standard 80/20 blend formulation: 0.8g Viton GLT, 0.2g FES, 0.2g Austin Black, 0.1g MT Black, and 0.04g 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" x 3"). The standard 80/20 blend formulation in these cases used 25g Viton GLT, 6.25g FES, 6.25g Austin Black, 3.125g MT Black, and 1.25g 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 8

TIMETABLE FOR BLEND FORMULATION

<u>OPERATION</u>	<u>TIME REQUIRED</u>	<u>COMMENTS</u>
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, $\text{Ca}(\text{OH})_2$, 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 agent Luperc 101XL is weighed		
Addition of curing agent to blend compound	7 min (large scale) 4 min (microscale)	Water-cooling of rolls important to prevent curing on the mill.

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