Fluorocarbon Rubbers for High Temperature Service

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At a meeting of the London Section of the Institution of the Rubber Industries, held at 26 Portland Place, London, on the 4th June, 1957, the following paper was read by Mr. Oesterling.

The development of modern weapons and the varied climatic military operations continually extend the operating range of temperatures for elastomers. These rubbers must also possess resistance to fuels, chemicals and strong oxidisers because applications in many cases require direct contact with such liquids as well as exposure to extreme high and/or low temperatures. Several years ago the Quartermaster Corps, U.S. Army, initiated a research programme in co-operation with the M. W. Kellogg Company and the University of Florida to develop new elastomers for this purpose from fluorine containing compounds. Significant progress has been achieved, both in the low and in the high range of temperature service. This discussion, however, will be limited to the new fluorinated elastomers developed under this programme possessing thermal stability at high temperatures. Specifically, three saturated fluorinated rubbers containing vinylidene fluoride ($CF_2 = CH_2$) will be described. Two are copolymers of vinylidene fluoride and chlorotrifluoroethylene ($CFCl = CF_2$) with ratios of 50 : 50 and 70 : 30 respectively. The third is a 30 : 70 copolymer of perfluoropropene ($CF_3CF = CF_2$) and vinylidene fluoride.

The first two rubbers (50 : 50 and 70 : 30 copolymers of vinylidene fluoride and chlorotrifluoroethylene) are commercially available and are known by the trade names KEL-F Elastomers 5500 and 3700 respectively. The third is still an experimental rubber (25 lb. have been produced in the laboratory) and is designated as Fluorocarbon Elastomer 214; however, plans are being made to produce it commercially.

KEL-F ELASTOMER 5500 (50 : 50 copolymer)

Of the three rubbers, KEL-F Elastomer 5500 was the first developed. Consequently, it was compared with other commercially available rubbers with regard to physical and chemical properties. The chemical properties of the above compound as compared with typical formulations of commercial rubbers are shown in Table 1.

TABLE 1

COMPARISON OF KEL-F ELASTOMER 5500 WIMH COMMERCIAL RUBBERS

Types of tests	KEL-F Elastomer 5500	Buna-N	Neoprene	Hypalon	Butyl
Retention of original tensile strength after immersion for 2 hours in WFNA 15 72° F.*	100%	Disintegrates in 30 min.	Disintegrates in 1 min.	20%	Disintegrates in 30 min.
Retention of original tensile strength after exposure to 0·013% ozone for 6 hours at 72° F. Rubbers stretched 30%.	100% Note: GR-S breaks within 20 min.	Not tested	Not tested	100%	70%
Volume change after immersion in type III fuel for 24 hours at 72° F.†	4%	20%	60%	60%	200%
Volume change after immersion in fuming H_2SO_4 for 24 hours at 72° F.	0·5%	Charred	Charred	Charred	Not tested
Flame retardance‡	Excellent	Poor	Good	Fair	Poor

* WFNA—White fuming nitric acid.
† Type III fuel is a 70 : 30 mixture of iso-octane and toluene.
‡ Samples held at 90° angle to flame and then removed from flame. Flame in KEL-F Elastomer was extinguished almost immediately after removal from flame. Buna-N burned indefinitely.

From these results, it could be seen that KEL-F Elastomer 5500 has better resistance to strong oxidisers such as nitric and sulfuric acids, to hydrocarbon fuels, and to ozone than any of the commercial rubbers. It also possesses better flame-retardant characteristics than the best flame-retardant commercial rubber, Neoprene. Conroy *et al.*[1] and Montermoso and Griffis[2] showed that KEL-F Elastomers are chemical resistant and are superior in thermal stability to any chemical resistant rubbers commercially available.

TABLE 2

Tests	KEL-F Elastomer 5500	KEL-F Elastomer 3700
Stiffness, Gehman T_5* ..	+32° F.	+7° F.
Volume swell in Fuel III† after 7 days at room temp.	30%	14%

* Gehman T_5 is the temperature in which the rubber is five times as stiff as at room temperature.
† Fuel III is a 70 : 30 mixture of isooctane and toluene.

KEL-F ELASTOMER 3700

This rubber is a 30 : 70 copolymer of chlorotri-fluoroethylene and vinylidene fluoride. The physical properties of KEL-F Elastomers 5500 and 3700 are practically the same except that the latter possesses slight superiority in low temperature flexibility and in resistance to hydrocarbon fuels as shown in Table 2.

FLUOROCARBON ELASTOMER 214[3]

Recently, a new fluorocarbon rubber, Fluorocarbon Elastomer 214, was developed under the U.S. Army Quartermaster Corps programme. It is a 70 : 30 copolymer of vinylidene fluoride and perfluoropropene. In our early tests it showed combined chemical resistance and thermal stability superior to those of the KEL-F Elastomers. More complete evaluation of Fluorocarbon Elastomer 214 was carried out in our laboratory with emphasis on determining those properties. The KEL-F Elastomer 3700 was used as the standard for basis of comparison.

Compounds were made from Fluorocarbon 214 and from Elastomer 3700 using curing systems suitable for both. Three types (peroxide, amine, and carbamate) of curing systems were chosen. The formulations used are shown in Table 3.

TABLE 3

FORMULATIONS

	Peroxide cure		Amine cure		HMDA-Carb. cure	
	214	3700	214	3700	214	3700
Fluorocarbon 214 ..	100		100		100	
KEL-F Elastomer 3700		100		100		100·0
Hi-Sil 202	10	10	15	10	10	8·9
Zinc oxide	5	5	10	5	5	4·4
Dyphos*			10	10	10	8·9
Cadox BCP†	9	9				
Triethylene tetramine			2	2·5		
HMDA-Carbamate‡ ..					2	2·7
Press cure, min./° F.	60/240	60/240	30/320	60/260	30/320	30/320
Oven cure Hours/F...	16/250	16/250	16/350	16/250 16/300 16/350	16/350	16/350

* Dibasic Lead Phosphite.
† 35 per cent. Benzoyl Peroxide, 65 per cent. Calcium Phosphate.
‡ Inner salt of Hexamethylene Diamine.

After moulding and curing, the physical properties of the vulcanisates at room temperature were determined. The tensile strength and elongation were determined with an Instron tester using dumbbell-shaped specimens $3\frac{3}{4}$ in. in length with a constricted section $1\frac{1}{8}$ in. long and $\frac{1}{8}$ in. wide. The physical properties of the vulcanisates at room temperature are shown in Table 4. In the peroxide cure, the two elastomers are about the same; in the amine and carbamate cures, Elastomer 3700 has higher tensile strength; however, by variation in the formulations, it is believed that improvement in tensile strength of 214 may be obtained.

TABLE 4

PHYSICAL PROPERTIES AT ROOM TEMPERATURE

	Peroxide cure		Amine cure		HMDA carb. cure	
	214	3700	214	3700	214	3700
Tensile strength, p.s.i.	2830	2980	1680	2140	1710	2640
Ultimate elongation, %	500	240	150	340	265	395
Stress at 300% elongation, p.s.i.	1160			2110		1830
Hardness, shore A, 5 sec. reading	65	62	80	69	65	65

CHEMICAL RESISTANCE AT ROOM TEMPERATURE

For tests in chemical resistance at room temperature, the vulcanisates were immersed in a number of organic fluids and solvents for 48 hours and the per cent. volume swell determined. The following liquids were selected: (1) fluid III, a hydrocarbon fuel which is typical of the gasoline type fuels to which hoses and gasketing materials are exposed or in direct contact, (2) SAE 50 motor oil, used in automotive and transportation vehicles where it is in contact with numerous rubber parts, (3) turbo oil 15, a diester oil, and (4) MLO-O-8200, a silicate diester oil. The last two liquids are high boiling hydraulic fluids used at elevated temperatures. The result of tests conducted with these fluids are shown in Table 5.

TABLE 5

PER CENT. VOLUME INCREASE AFTER 48 HOURS AT 75±1° F.

	Peroxide cure		Amine cure		HMDA Carb. cure	
	214	3700	214	3700	214	3700
Fluid III*	1	5	1	5	0	4
SAE 50 motor oil	0	1	0	0	−1	0
Turbo oil 15†	−2	49	−2	54	−2	49
MLO 8200‡	−2	−1	−1	−2	0	−3

* A 70/30 mixture by volume of Isooctane/Toluene.
† A diester oil.
‡ A silicate ester oil.

It can be seen from this table that Fluorocarbon 214 is equal or slightly superior to 3700 in fluid III, SAE 50, and MLO 8200. However, in turbo oil the fluorocarbon 214 is definitely superior. Fluorocarbon 3700 swells about 50 times as much as the 214 in diester oil. This difference of the two elastomers in swelling resistance to diester oil will be reflected in tensile strength of the two rubbers after exposure to this medium.

TABLE 6

PHYSICAL PROPERTIES AFTER 6 HOURS IN RFNA AT 75±1° F.

	Peroxide cure		Amino cure		HMDA Carb. cure	
	214	3700	214	3700	214	3700
Tensile strength, p.s.i.	1540	1780	1250	1150	1360	1450
Ultimate elongation, % ..	485	280	195	310	275	390
Stress at 300% elongation, p.s.i.	710			1110		950
Hardness, shore A, 5 sec. reading	65	57	76	63	60	57

Resistance to strong oxidising agents was determined by immersing tensile test specimens in red fuming nitric acid for 6 hours. Red fuming

nitric acid was chosen as a medium for test because it is planned to use this rubber as coating for fabrics in protective suits for liquid propellant handling. The changes in physical properties of the vulcanisates are shown in Table 6. In all three cures, at least 50 per cent. of the original tensile strengths are retained showing these fluorocarbon rubbers to have excellent resistance to red fuming nitric acid.

HIGH TEMPERATURE CHARACTERISTICS

To determine high temperature stability, test samples of each elastomer with each curing system were conditioned at high temperatures both in air and in various liquids. The samples were hung inside 38 by 300 millimeter test tubes which were stoppered and fitted with glass condensing tubes. Where SAE 60 motor oil, turbo oil 15, or MLO-8200 was used, sufficient liquid was added to completely cover the samples. The tubes were then inserted in the cored holes of an aluminium block heater. Fluid III test tubes were fitted with water-cooled reflux condensers and placed into an oil-bath. The highest temperature used with each medium was determined by the safe operating range of the medium itself. In air and in MLO-8200 temperatures of 400° F., 500° F., 550° F. and 600° F. were used. The turbo oil 15 was used at 400° F. and 500° F., and SAE 50 motor oil at 400° F. Samples in fluid III (isooctane-toluene mixture) were heated to 220° F., the boiling point of the liquid. Exposure period chosen was 70 hours. Samples exposed to heated air were tested 16 hours after removal from the heat; liquid immersed samples, 4 hours after removal from the heated liquid.

TABLE 7

PHYSICAL PROPERTIES AFTER 70 HOURS IN AIR

	Peroxide cure		Amine cure		HMDA-Carb. cure	
	214	3700	214	3700	214	3700
400° F.						
Tensile strength, p.s.i.	2350	2970	1500	960	1700	1320
Ultimate elongation, % ..	475	435	190	355	310	540
Stress at 300% elongation, p.s.i.	1310	1730		1110	1630	1150
Hardness, shore A, 5 sec. reading	64	64	81	75	66	67
500° F.						
Tensile strength, p.s.i.	1470		1110	380	1000	480
Ultimate elongation, % ..	715	Charred	190	75	395	40
Stress at 300% elongation, p.s.i.	730				820	
Hardness, shore A, 5 sec. reading	63	100+	77	81	64	81
550° F.						
Tensile strength, p.s.i.	210		690	Broke	440	Broke
Ultimate elongation, % ..	750		80	on	145	on
Stress at 300% elongation, p.s.i.	140			bending		bending
Hardness, shore A, 5 sec. reading	56		86	100+	71	100+
600° F.						
Tensile strength, p.s.i.	Charred		Broke		Broke	
Ultimate elongation, % ..	Cracked		on		on	
Stress at 300% elongation, p.s.i.			bending		bending	
Hardness, shore A, 5 sec. reading	—	—	—	—	—	—

Physical properties after 70 hours exposure in air at temperatures up to 600° F. are given in Table 7. The results show that in air Fluorocarbon 214 is superior in heat resistance to KEL-F Elastomer 3700. If we arbitrarily chose minimum tensile strength of 500 p.s.i. as the serviceability limit after those exposures, then we can state that the amine cure of Elastomer 3700 is serviceable after 70 hours exposure in air at 475° F. while the 214 Elastomer is still useable after the same exposure at 575° F., a difference of 100° F.

The effects of 70 hours immersion in MLO 8200, silicate diester oil, are shown in Table 8. In the three types of cures, Elastomer 214 shows an advantage of at least 50° F. in thermal stability.

TABLE 8

PHYSICAL PROPERTIES AFTER 70 HOURS IN MLO 8200

	Peroxide cure		Amine cure		HMDA-Carb. cure	
	214	3700	214	3700	214	7300
400° F.						
Tensile strength, p.s.i...	1900	1540	1470	1670	1630	1660
Ultimate elongation, %	610	140	180	205	270	260
Stress at 300% elongation, p.s.i.	740					
Hardness, shore A, 5 sec. reading	62	65	79	76	66	66
500° F.						
Tensile strength, p.s.i...	490	Samples	920	Brittle	440	Samples
Ultimate elongation, %	130	and	30		25	and
Stress at 300% elongation, p.s.i.		oil				oil
Hardness, shore A, 5 sec. reading	55	Charred	70	100+	65	Charred
550° F.						
Tensile strength, p.s.i...	470		Broke		Oil	
Ultimate elongation, %	30		on		Charred,	
Stress at 300% elongation, p.s.i.	Oil charred		Bending		Samples	
Hardness, shore A, 5 sec. reading	77		100+		Brittle	
600° F.						
Tensile strength, p.s.i...	Samples					
Ultimate elongation, %	and					
Stress at 300% elongation, p.s.i.	oil					
Hardness, shore A, 5 sec. reading	Charred					

TABLE 9

PHYSICAL PROPERTIES AFTER 70 HOURS IN TURBO OIL 15

	Peroxide cure		Amine cure		HMDA-Carb. cure	
	214	3700	214	3700	214-C3700	
400° F.						
Tensile strength, p.s.i...	2290	680	1090	120	1770	160
Ultimate elongation, %	745	240	315	455	325	500
Stress at 300% elongation, p.s.i.	470		1120	150	1550	160
Hardness, shore A, 5 sec. reading	53	28	74	14	59	14
500° F.						
Tensile strength, p.s.i...	960	Samples	580	20	630	Samples
Ultimate elongation, %	1110	disin-	20	10	75	disin-
Stress at 300% elongation, p.s.i.	350	tegrated				tegrated
Hardness, shore A, 5 sec. reading	55		80	0	62	

Immersion of the test samples for 70 hours in turbo oil 15, a diester oil, have decided effects on the physical properties. This is shown in Table 9.

The elastomer 214 is still strong and useable after 70 hours in this liquid at 500° F. (Figs. 5, 6 and 7.) There is an advantage of at least 100° F. of the Elastomer 214 over the 3700 in resistance to diester oil. This marked difference of the two elastomers in physical properties after exposure is reflected in their resistance to swelling in turbo oil 15 as previously shown in Table 5.

Tables 10 and 11 show the effect of 70 hours immersion at 400° F. in SAE 50 motor oil and at 220° F. in fluid III (a mixture of isooctane and toluene) respectively. Both elastomers, regardless of type of cure, have excellent resistance to SAE 50 motor oil and to fluid III. At least 50 per cent. of the original physical properties are retained in every case.

TABLE 10

PHYSICAL PROPERTIES AFTER 70 HOURS IN SAE 50 MOTOR OIL

	Peroxide cure		Amine cure		HMDA-Carb. cure	
	214	3790	214	3700	214	3700
400° F.						
Tensile strength, p.s.i...	2190	2150	1550	1970	1690	2070
Ultimate elongation, %	435	215	165	280	225	280
Stress at 300% elongation, p.s.i.	1350					
Hardness, shore A, 5 sec. reading	64	64	81	76	64	66

TABLE 11

PHYSICAL PROPERTIES AFTER 70 HOURS IN FLUID III

	Peroxide cure		Amine cure		HMDA-Carb. cure	
	214	3700	214	3700	214	3700
220° F.						
Tensile strength, p.s.i...	1810	1500	1130	680	1110	1130
Ultimate elongation, %	515	225	205	195	200	385
Stress at 300% elongation, p.s.i.	650					880
Hardness, shore A, 5 sec. reading	58	54	68	55	59	55

SUMMARY

The properties of three fluorine-containing rubbers developed under the rubber programme of the Quartermaster Corps, U.S. Army have been presented. KEL-F Elastomer 5500 possesses chemical resistance and thermal stability at high temperatures superior to any chemical resistant commercial rubbers. KEL-F Elastomers 5500 and 3700 have practically the same chemical and physical properties except that the latter possesses slight superiority in low temperature flexibility and in resistance to hydrocarbon fuels.

Fluorocarbon Elastomer 214 is superior to Elastomer 3700 after exposure at high temperatures in air, hydrocarbon fuels, motor oil and diester oil. Both elastomers have excellent resistance to red fuming nitric acid at room temperature.

Compared with other types of fuel and chemical resistant rubbers Fluorocarbon Elastomer 214 has superior resistance to oils, fuels, and strong oxidisers. It has an advantage of at least 150° F. in thermal stability at high temperatures. Fluorocarbon 214 is serviceable at 500°F.

for extended periods of time and, in some cases, at 600° F. for limited short periods.

The development of this rubber is of major importance, especially to the military, since it possesses a combination of characteristics needed in a rubber. Fluorocarbon research is being actively pursued by the Quartermaster Corps.

References

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