Tetrafluoroethylene-Propylene Copolymer (Aflas®): New Technology, New Uses

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Tetrafluoroethylene-propylene copolymer (Aflas) is a new type of elastomer with a unique combination of high temperature, electrical, and especially chemical resistance properties.

The structure of this elastomer (copolymer of tetrafluoroethylene and propylene) provides heat, chemical, and electrical resistance properties different from other elastomers. Effective utilization of the polymer is enhanced by recognition of its unique properties and differentiation from previously available commercial elastomers. This paper provides an overview of its properties; discusses areas of application; and outlines processing characteristics.

There are three grades of the polymer and guidelines to polymer selection and compounding will also be briefly discussed for applications in oilfield, chemical processing, automotive, aerospace, and general industrial environments.

The elastomer is produced solely by Asahi Glass Company, Ltd., and sold under the brand name "Aflas" (registered trademark of Asahi Glass Company, Ltd.). Throughout this paper it will be referred to as TFE/P. Technical development, application assistance, and distribution in North America are performed by Xenox, Inc., Houston, Texas. In the U.K., the elastomer is distributed by a Xenox designated representative, Anchor Chemical (UK), Ltd.

There are three different molecular weight varieties of the TFE/P elastomer: 150E is the lowest molecular weight used for high speed extrusions; 150P intermediate weight is used for most molded and extruded goods; 100H high molecular weight is used where extrusion and gas blistering resistance to high pressures is required (primarily oilfield uses).

The specific gravity of the TFE/P elastomer is 1.55 and the appearance is dark brown. It is supplied in sheet form and storage life is excellent. The 150E and 150P varieties are soluble in Freon TF and, under certain conditions, in ethyl acetate. The elastomer is peroxide cured with triallylisocyanurate (TAIC) the required co-agent.

Chemical Resistance

An interesting property of the TFE/P elastomer is its resistance to a relatively broad range of chemicals. This is particularly helpful when combinations of chemicals are encountered, when chemical exposure of rubber parts is not closely controlled, and when additive packages alter the chemical nature of a base fluid — i.e., additives in SF rated engine oils.

Generally speaking, the TFE/P offers resistance to acids, bases, steam/hot water, hydraulic fluids of all types, brake fluids, oils and lubricants, sour (H_2S) oil and gas, amine corrosion inhibitors, oxidizing agents, bleaches, alcohol, and various industrial solvents. It provides good resistance to radiation and excellent resistance to weathering and ozone. Indications of its chemical resistance are shown in Table 1.

Of particular note is its resistance to: (1) oil and high temperature 260° C) steam (encountered in steam injection oilwells); (2) aryl/alkyl phosphate ester hydraulic fluids used in commercial aircraft and all other types of hydraulic fluids as well as oils, lubricants, and jet fuel; (3) SF rated engine oils which contain additive packages that attack previously used high temperature elastomers; (4) engine coolants with corrosion inhibitor additives; (5) sour (H_2S) oilwell environments and amine corrosion inhibitors which embrittle fluorocarbon elastomers; (6) acidic *and* basic environments which can occur as acid processing steps are followed by basic neutralizing steps or when pollution control systems are treated with lime to neutralize acids in the system; and (7) brake fluid *and* mineral oil in automotive/truck braking systems which previously required two different types of elastomeric seals.

Table 1 — Indicators of TFE/P Chemical Resistance

Chemical	Test Conditions °C	Test Conditions Days	Volume Change (%)
Acetone	21	7	50.0
Ammonium Hydroxide (28%)	70	3	3.2
ASTM Oil #1	100	3	1.8
ASTM Oil #3	100	3	7.9
Gasoline	21	7	25.0
Methyl alcohol	21	7	.2
Nitric acid fuming	21	180	15.2
Phosphate ester hydraulic fluid (allyl/alkyl)	100	3	14.0
Sodium hydroxide 20%	100	3	2.0
Steam	288	4	1.6
Toluene	21	7	41.0
Water	100	3	1.1

High Temperature Properties

In terms of retention of physical properties after aging in air, the TFE/P elastomer provides long term service at 200° C and progressively shorter term service up to a practical limit of 288° C. There are instances, however, of the elastomer passing service requirements for temperature spikes above 320° C.

Recent compounding and polymer improvements have significantly improved compression set properties such that O-ring (25.4 mm x 3.5 mm) Method B compression set values of 25% after 70 hours at 200°C and 45% after 70 hours at 260°C are obtained. An example of a low compression set compound is Compound C of Table 2. The use of 100H polymer, high levels of TAIC, and Austin black are all helpful in reducing compression set of the TFE/P polymer.

The use of high molecular weight polymer (100H) and special compounding has also resulted in improved retention of properties at high temperature. For instance, tensile stengths of 6.9 MPa (1000 psi) are now obtained at 175C. The same techniques have been used to improve extrusion resistance for oilfield applications at high temperatures. Compounds D and E of Table 2 are examples of extrusion resistant formulations. Higher levels of Ricon 153 may be used to further increase extrusion resistance. AC 602 from Allied Corporation is used to improve compound flow rate during molding of these high durometer compounds.

High temperature applications of TFE/P and other elastomers often occur in various chemicals. Accordingly, the TFE/P elastomer is generally distinguished from other elastomers by its high temperature chemical resistance rather than by its high temperature air aging.

The TFE/P provides high values of electrical resistance — most notably at high temperatures. Combined with heat and chemical resistance this property is useful in many areas such as electrical connectors and boots and wire and cable insulation or sheathing in corrosive environments. Illustrative values of resistance are shown in Table 3.

Table 2 — TFE/P Compound Examples

	A (phr)	B (phr)	C (phr)	D (phr)	E (phr)
Aflas 100H	—	—	100.0	100.0	100.0
Aflas 150P	100.0	100.0	—	—	—
TAIC (75% dispersion)	7.5	7.5	12.0	7.5	10.0
Vul-Cup 40 KE*	2.5	2.5	5.0	7.0	5.0
Carnauba Wax	—	—	1.0	1.5	1.5
Ricon 153 (70% dispersion)**	—	—	—	7.5	—
Sodium Stearate	2.0	2.0	—	—	—
MT Black (N990)	28.0	—	—	—	—
FEF Black (N550)	—	25.0	—	20.0	—
AC 602***	—	—	—	—	2.0
Austin Black	—	—	25.0	15.0	—
Aerosil R972****	—	—	—	15.0	—
SAF (N119)	—	—	—	—	30.0
SRF (N774)	—	—	—	—	50.0

Cure - 30 mins. at 165C Postcure - 16 hrs. at 200C

Vulcanized Properties

	A	B	C	D	E
Hardness (Shore A/D)	70A	83A	80A	95A	65D
Elongation (%)	160	110	150	90	50
50% Modulus (psi)	—	—	980	1800	2300
Tensile Strength (psi)	2500	2600	2200	3000	2300

*Peroxide from Hercules, Inc.
**High vinyl 1, 2 polybutadiene from Colorado Chemical Specialties
***Low MW polyethylene from Allied Corp., process aid to improve flow
****Fumed, hydrophobic silica from DeGussa Corp.

Table 3 — TFE/P Electrical Properties (Vulcanized Polymer)

Volume Resistivity (ohms cm, 500 volts dc)		
at 21C	3.0×10^{16}	
at 200C	1.7×10^{13}	
Dielectric Constant	60 hz	10 hz
at 21C	2.5	2.6
at 150C	3.0	2.8
Dielectric Strength (ASTM D 149, volts/mil)		
at 21C	580	
at 200C	200	

Compounding and Processing

Rubber parts of TFE/P are made like any other rubber part — i.e., compression, transfer, injection molding. Compounds are mixed on open mills or internal mixers. Curing temperatures and times are, of course, determined by peroxide types, part cross section, etc. Time/temperature relationships most commonly fall between 30 minutes at 165° C and three minutes at 195° C. Special peroxide types and/or cure accelerators permit open steam curing or press cures at 130° C.

Very specialized compounds have also been developed such as those using chopped and/or milled fiberglass or other fibrous fillers which can produce high tensile strengths — i.e., 34.5 MPa (5,000 psi) — with excellent abrasion resistance. Illustrative examples of TFE/P compounds are shown in Table 2.

The 150P polymer grade is generally used for solution coating fabrics such as fiberglass; applications include V-rings, U-cups, etc. Solutions containing 20% to 30% solids are commonly used. If small particles (i.e., the size of pencil erasers) of the compound can be obtained, a high shear mixer and high purity (99%) ethyl acetate alone can be used to develop the desired solution in about one hour.

If small particles cannot be obtained, a mixture of Freon TF and ethyl acetate is required. In this instance, particles (i.e. 5 cm square by .5 cm thick) of the TFE/P compound are first soaked 18 hours in ethyl acetate. A drum impeller is then inserted and the mixture is stirred about 4 hours until a suspension is formed. At this point, Freon TF is added until the desired solution is formed. It takes about 3 hours, for example, to form a 30% solution.

The ethyl acetate/small particle procedure is generally preferred to avoid possible difficulties with HF evolution from residual Freon TF on the coated fabric at high temperatures.

Polymer Blends

A discussion of blends with other elastomers is beyond the scope of this paper, but blends have been used for several years in order to modify TFE/P or other elastomer properties (low temperature, chemical resistance, processability, etc.) or to reduce the cost of the polymer. The types of elastomers that have been blended with TFE/P include siicone, fluorosilicone, ethylene-propylene, ethylene-propylene-diene, and fluorocarbon elastomers.

Areas of Applications

Although applications in corrosive oilfield environments received early publicity, usage of TFE/P has now spread into general industry as well as the chemical and agrichemical, automotive, and aerospace industries.

Oilfield. The ability of TFE/P to resist a wide range of chemicals has been particularly beneficial in this industry. Oilfield rubber parts can be exposed to many fluids and gases including oil, sour (H_2S) oil and gas, amine corrosion inhibitors, steam/hot water, acids, CO_2, diesel and water based drilling and completion fluids, and high pH completion fluids.

This diversity of fluids and gases and the uncertainty about when they might be encountered has placed a new burden on oilfield rubber materials. For instance, fluorocarbon elastomers did an excellent job of coping with higher temperatures, but embrittled when amine corrosion inhibitors were used to treat sour wells. They also encountered difficulties in high pH completion fluids and in high temperature steam.

The TFE/P elastomer, however, has the potential to resolve these difficulties since it is resistant to all the previously mentioned oilfield fluids and gases. It can resist combinations of sour oil or gas *and* amine corrosion inhibitors; oil *and* high temperature steam; drilling fluids *and* amine inhibitors. Examples of TFE/P resistance to various oilfield chemicals are shown in Table 4.

It is interesting to note that oilfield formulations of TFE/P maintain comparable or better percentages of original tensile strength after immersion in diesel based drilling fluids compared to fluorocarbon elastomers while showing higher volume swell. Oilfield use in diesel based fluids have demonstrated that the TFE/P elastomer performs well in this media.

Earlier oilfield usage of the 150P TFE/P polymer showed it has the necessary chemical and heat resistance but not the strength required to resist extrusion under high pressure and high temperature conditions. Fabric reinforced parts provided one solution, but were not always practical nor could backups be used in every application (i.e., retrievable packers). In response to the need for high strength TFE/P, the 100H polymer was developed. This is a higher molecular weight variety of TFE/P and recent formulations based on this polymer have more than tripled the extrusion resistance of 150P formulations. However, even this improvement can be defeated under very high pressure conditions where wide extrusion gaps are present. In these instances backups or some reinforcements such as fabric in the rubber are required to maintain a seal.

The TFE/P elastomer has also shown high resistance to the blistering or splitting that can occur when pressure is suddenly lost in a well after rubber parts have been exposed to high pressure CO_2 or gas. If this situation is anticipated, high durometer 150P formulations are required and in extreme cases, high durometer 100H formulation since 100H is more resistant to blistering than 150P.

In terms of resistance to high temperature, the TFE/P elastomer is rated long-term for 200° C. However, there are several instances of oilfield usage in the range of 288° C for shorter periods of time.

In addition to the heat and chemical resistance of this elastomer, its ability to maintain high values of electrical resistance at high temperatures has proven beneficial in downhole instrumentation activities.

Typical applications involving the TFE/P elastomer in the oilfield include: packers; seals used in drill bits, valves of various types, and other oilfield equipment; packing, both homogeneous and fabric reinforced; diaphragms for pumps and valves; and boots and connectors used in downhole instrumentation.

Chemical/Agrichemical. Again, the wide range of chemical resistance is of value since many processes require exposure to combinations of chemicals. For instance, an acid treatment may be followed by a neutralizing high pH solution. Often it is more the chemical resistance of the TFE/P elastomer than its high temperatue resistance which leads to usage in this industry. Although in many applications the TFE/P elastomer does not exhibit the best resistance to one fluid, it may be the only elastomer which can exhibit acceptable resistance to a combination of chemicals.

The types of applications the TFE/P elastomer is specified for in this indus-

Table 4 — TFE/P Resistance to Oilfield Media
(Compound D)

		Aged Properties		
	Shore A	Tensile Strength	Elongation at Break	Volume Change
		(psi)	(%)	(%)
		(psi)	(%)	(%)
Aged 100 hrs in 550F Steam	93	1950	110	1.6
Aged 100 hrs at 400F wet sour gas (35% H_2S, 50% CH_4, 15% CO_2, water)	90	2000	90	3.5
Aged 336 hrs at 324F in water and 1% NACE A amine inhibitor	89	1800	170	7.0
Aged 70 hrs at 400F in diesel drilling mud and 5% NACE B amine inhibitor	75	2100	140	26.3
High fluorine fluorocarbon, 95 Shore A				
Original properties	95	2300	80	
Aged properties	82	828	50	11.2
Aged 70 hrs at 300F in water drilling mud and 5% NACE A	90	2900	130	1.9
High fluorine 95A fluorocarbon as above				
Aged properties	62	815	45	23.2

Table 5 — TFE/P Resistance to Chemicals
(Compound A)

		Aged Properties		
	Shore A	Tensile Strength	Elongation at Break	Volume Change
		(psi)	(%)	(%)
Aged 72 hrs at 158F in 37% hydrochloric acid	68	1425	179	7.0
Aged 72 hrs at 73F in 60% nitric acid	69	2350	152	0.0
Aged 72 hrs at 212F in 50% sodium hydroxide	67	2525	187	2.0
Aged 72 hrs at 212F in 60% sulfuric acid	71	2675	166	.4
Aged 48 hrs at 158F in 67% hydroxyacetic acid, 7% formaldehyde, 1% sulfuric acid, 25% water	69	2175	154	0.0