IMPROVED SEAL MATERIALS FOR USE IN FOOD AND PHARMACEUTICAL PROCESSES

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Introduction

Elastomers, because of their inherent resiliency, are capable of providing excellent sealing for connections in piping, pumps, and processing equipment in general. Different types of elastomers, however, exhibit significantly different degrees of resistance to heat and chemicals, and choosing the correct elastomer for a given sealing application is critical for obtaining the best possible performance. Ethylene-propylene rubber (EPDM), for example, exhibits excellent resistance to water and steam, but provides very poor resistance to many aliphatic and aromatic hydrocarbons. Conversely, silicone rubber (VMQ) exhibits acceptable resistance to many hydrocarbons, but has relatively poor resistance to steam.

Viton® fluoroelastomer (FKM), in addition to providing outstanding resistance to high temperatures, has also long been recognized as exhibiting excellent resistance to a very broad range of chemicals and fluids, as indicated in the examples shown in Table I.

Table I
General Chemical Resistance of Various Elastomers*
(Los Angeles Rubber Group)

	EPDM	VMQ	FKM
Amyl Alcohol	1	4	2
Wet Chlorine	3	4	1
Corn Oil	3	1	1
Hydrochloric Acid 37%	1	3	1
Peanut Oil	3	1	1
Rapeseed Oil	1	4	1

1 = 0 to 5% Swell: Recommended; Little or minor effect
2 = 5 to 10% Swell: Useful in most applications
3 = 10 to 20% Swell: Useful in some **static** (only) applications
4 = Not Recommended

*Volume change is commonly used as a general indicator of the ability of a vulcanizate to properly function as a seal. Relatively small (<10%) changes in the volume of a test specimen, after immersion in a fluid, generally indicates that the vulcanizate will exhibit little, or minor changes in (other) physical properties, such as tensile strength, modulus, and elongation, and should function well as a sealing material.

Fluid Resistance

Various fluoroelastomers have been available for a number of years that are in compliance with FDA food contact regulations (e.g., 21CFR177.2600), and which offer excellent resistance to a broad variety of different chemicals and fluids, including steam. However, some of the fluids that are used in cleaning processes are highly caustic in nature, and have a relatively severe effect on the fluoroelastomer materials that have commonly been available. Depending on the monomer content, and how the polymer is formulated and cured, some fluoroelastomers exhibit poor resistance to caustics, and it is perhaps because of this that fluoroelastomers have not been used more widely as a sealing material in the food and pharmaceutical industries.

It is important to know that, of the many different types of fluoroelastomer that are commercially available, the various polymers are comprised of different types and levels of monomers. These differences in composition can effect significant differences in the manner in which they behave in some fluids and chemicals. Examples of some of the more extreme differences between various types of fluoroelastomer, as measured by volume change, are outlined below, in Table II.

Table II
Differences in % Volume Change Between Types of Fluoroelastomer

Type of Fluoroelastomer:	Viton® A-401C	Viton® GF-600S	Viton® ETP-600S	TFE / Propylene
Methanol	**85**	**2**	**2**	**2**
Gasoline	**4**	**3**	**4**	**80**
Methylethylketone	**430**	**300**	**22**	**60**
Toluene	**20**	**6**	**4**	**40**

It is also important to understand that Viton® fluoroelastomer typically is sold as uncured, gum polymer, and not as finished parts. As outlined in Table III, the process of making a finished part requires incorporating various ingredients into the polymer, and then molding and curing the resulting mixture under heat and pressure into a final shape.

Table III
Processing Steps Involved in the Manufacture of FKM Parts

<table>
<tr><th>MIXING</th><th>PREFORMING</th><th>CURING</th><th>OVEN POSTCURE</th></tr>
<tr><td>Polymer(s)</td><td rowspan="5">Screw Extruder

Ram Extruder

Calendar</td><td rowspan="5">Injection Mold

Compression Mold

Transfer Mold

Autoclave

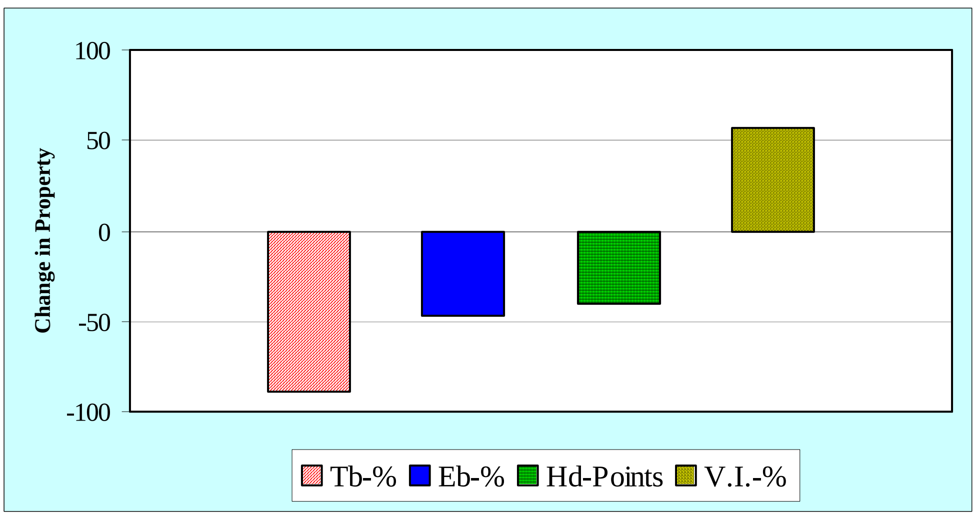
Salt Bath</td><td rowspan="5">2-24 Hrs, 200°-250°C

Useful for optimizing tensile strength, and resistance to compression set.</td></tr>
<tr><td>Accelerator & Crosslinker(s)</td></tr>
<tr><td>Acid Acceptor(s) [If required]</td></tr>
<tr><td>Filler(s): Carbon Black, Mineral Fillers</td></tr>
<tr><td>Process Aid(s)</td></tr>
</table>

The choice of filler type, like the choice of polymer, can have a substantial impact on the degree of resistance that a finished vulcanizate will exhibit in various fluids, particularly in the case of aqueous media, and mineral acids. Some mineral fillers, for example, are poor choices for applications that will involve exposure to sulfuric, nitric, or hydrochloric acids. Some, but not all, types of mineral fillers will dissolve in acid, resulting in significant losses in the strength of the part, and also in significant changes in the hardness and volume of the part and its ability to function as a seal.

Until early in 2006, the most commonly available types of fluoroelastomer that were approved for, or in compliance with FDA regulations regarding food contact use, were copolymers of vinylidene fluoride and hexafluoropropylene, and, optionally, tetrafluoroethylene. These polymers also were typically crosslinked with a bisphenol cure system that requires the incorporation of magnesium oxide and calcium hydroxide, at a level of about 6 to 8 percent by weight. These types of fluoroelastomer, represented by a compound based on Viton® A-401C in Figure 1, are subject to attack and degradation by high pH media. This attack is exhibited by relatively high volume swell and a substantial loss of tensile strength and hardness.

Figure 1
Viton® A-401C: Change in Physical Properties* After One Week At 100°C in 30% Potassium Hydroxide



*ASTM D412: Tb = Tensile Strength, Eb = Elongation ASTM D2240: Hd = Hardness, Shore A
ASTM D471: V.I. = Volume Increase

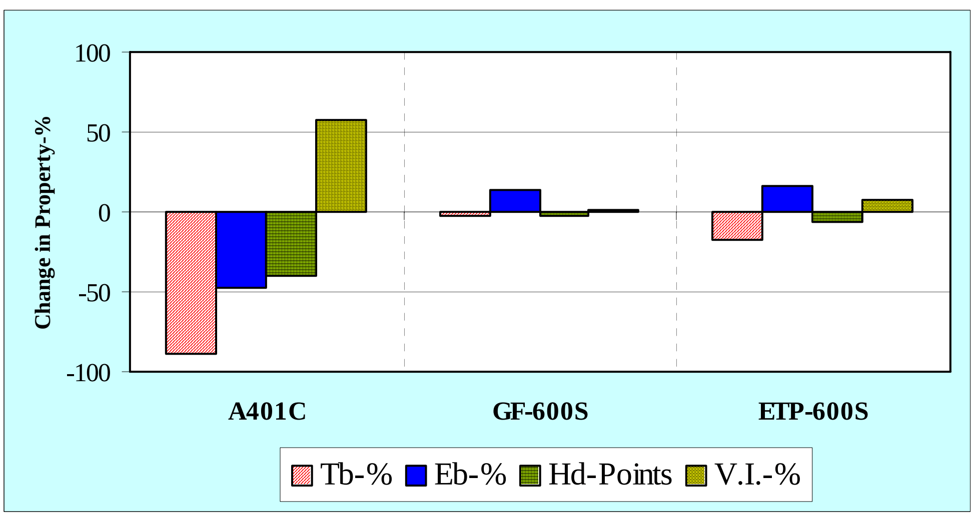
In 2006, Viton® GF-600S and Viton® ETP-600S were approved for repeated use in food contact applications, in all food types under all conditions of use, per FCN 00510 and FCN 00539, respectively. These polymers are cured with a peroxide crosslinking system, and compared to other types of elastomers, provide superior resistance to a wider variety of process and cleaning fluids, including, as shown in Figure 2, superior resistance to highly caustic fluids.

Compared to dipolymer FKMs, such as Viton® A-401C, Viton® GF-600S has a higher fluorine content (~70% vs ~66%) and is crosslinked with a peroxide curing system, as opposed to the bisphenol curing system used to cure Viton® A-401C. The unique peroxide cure system that is used in crosslinking Viton® GF-600S does not require the incorporation of any metal oxides/acid acceptors, and this results in inherently lower volume swell in aqueous media, and also, lower levels of extractible metals.

Like Viton® GF-600S, Viton® ETP-600S employs the same, unique peroxide cure system for crosslinking, but this polymer has a different monomer composition compared to other, more conventional fluoroelastomers. As mentioned earlier in this presentation, most commonly available fluoroelastomers are copolymers of vinylidene fluoride (VF2) and hexafluoropropylene (HFP), and, optionally, tetrafluoroethylene (TFE). Viton® ETP-600S is, instead, a copolymer comprised of ethylene, tetrafluoroethylene, and perfluoromethylvinyl ether. This monomer composition, unique among all commercially available fluoroelastomers, provides outstanding resistance to a considerably wider range of chemicals and fluids than can be provided for by conventional fluoroelastomers that are comprised of VF2/HFP or VF2/HFP/TFE.

Figure 1 showed an example of the deficiency of bisphenol-cured, dipolymer FKM, as represented by Viton® A-401C, in highly caustic solutions. Figure 2 compares the effect of the same fluid immersion, on the properties of vulcanizates made with Viton® GF-600S and Viton® ETP-600S versus the changes observed for the bisphenol-cure, dipolymer FKM.

Figure 2
Change in Physical Properties* for Vulcanizates Made with Viton® GF-600S and Viton® ETP-600S Compared to Viton® A-401C: After One Week At 100°C in 30% Potassium Hydroxide

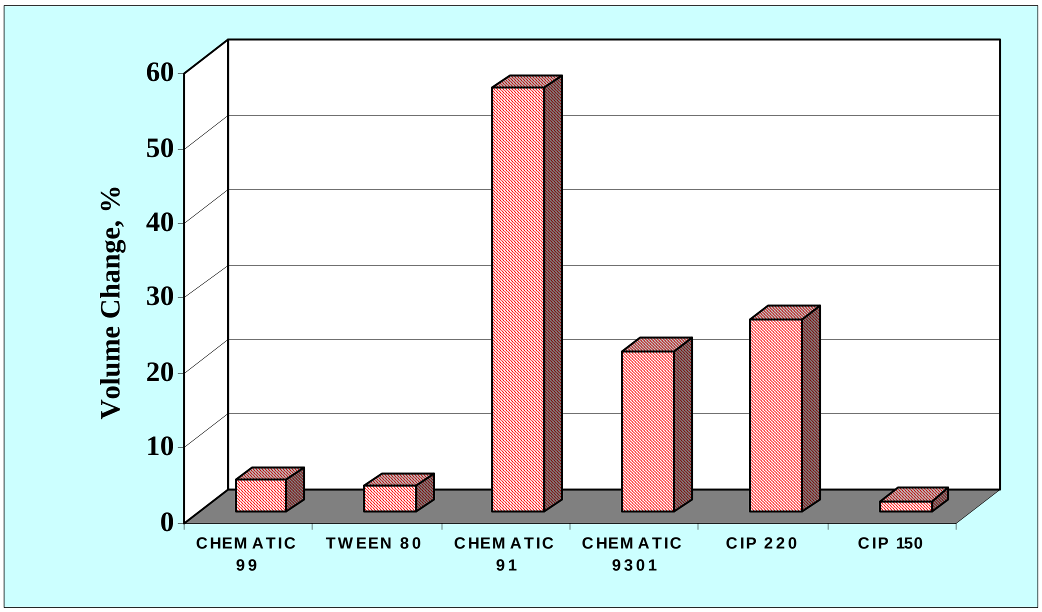


*ASTM D412: Tb = Tensile Strength, Eb = Elongation ASTM D2240: Hd = Hardness, Shore A
ASTM D471: V.I. = Volume Increase

Under the conditions shown in Figure 2, above, vulcanizates made with Viton® GF-600S and Viton® ETP-600S exhibit significantly smaller losses in tensile strength and hardness, and much smaller changes in elongation and volume, compared to vulcanizates made with the bisphenol-cure, dipolymer, Viton® A-401C.

The superior fluid resistance of these two fluoroelastomers is apparent in terms of resistance to property loss when immersed in various fluids that are used in cleaning food- and pharmaceutical-related process equipment. As mentioned earlier, it was found that some process cleaning fluids exhibited significant, deleterious effects on the properties of bisphenol-cured, dipolymer FKMs. Figure 3 illustrates the percent volume change for a vulcanizate made with Viton® A-401C that was aged in six different, commercially available cleaning fluids, for a period of 1008 hours, at 100°C.

Figure 3
Volume Change* for Viton® A-401C After 1008 Hours @ 100°C in Cleaning Fluids



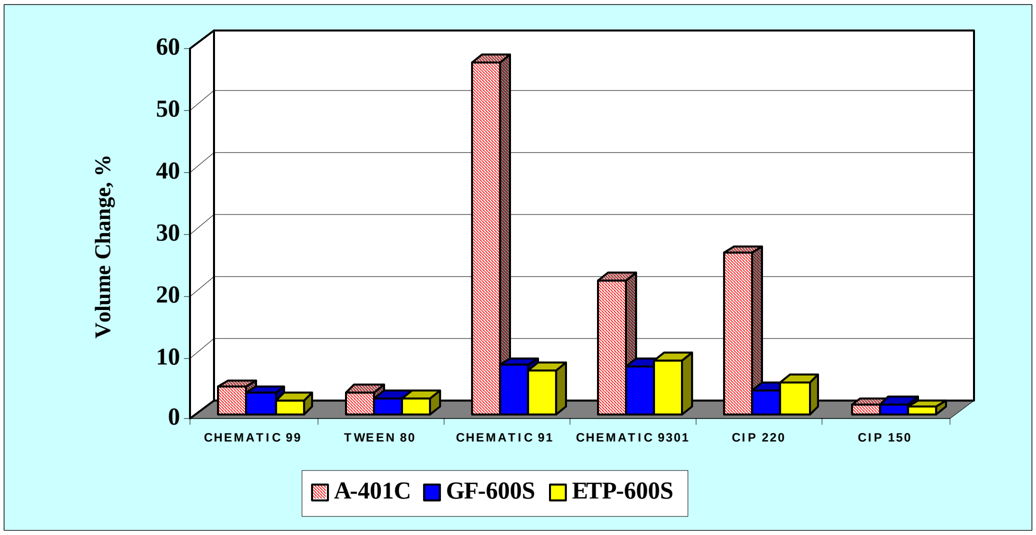
ASTM D471: V.I. = Volume Increase

As this Figure indicates, vulcanizates based on bisphenol-cure dipolymer FKM may work well in some process cleaning fluids, but may also be significantly degraded, when exposed to other, more aggressive fluids, such as Chematic™* 91 and 9301, and CIP™* 220.

When tested under the same conditions, vulcanizates made with Viton® GF-600S and Viton® ETP-600S exhibit significantly smaller changes in volume, as shown in Figure 4. This indicates that parts made with these polymers will perform well as seals in a much wider variety of cleaning fluids, compared to seals made with bisphenol-cure dipolymer FKM.

*Chematic™ - Registered trademark of the Dober Chemical Corporation, Midlothian, Illinois
*Tween™ - Registered trademark of Well, Naturally Products, Ltd., Surrey, B.C., Canada
*CIP® - Registered trademark of the Steris Corporation, Mentor, Ohio

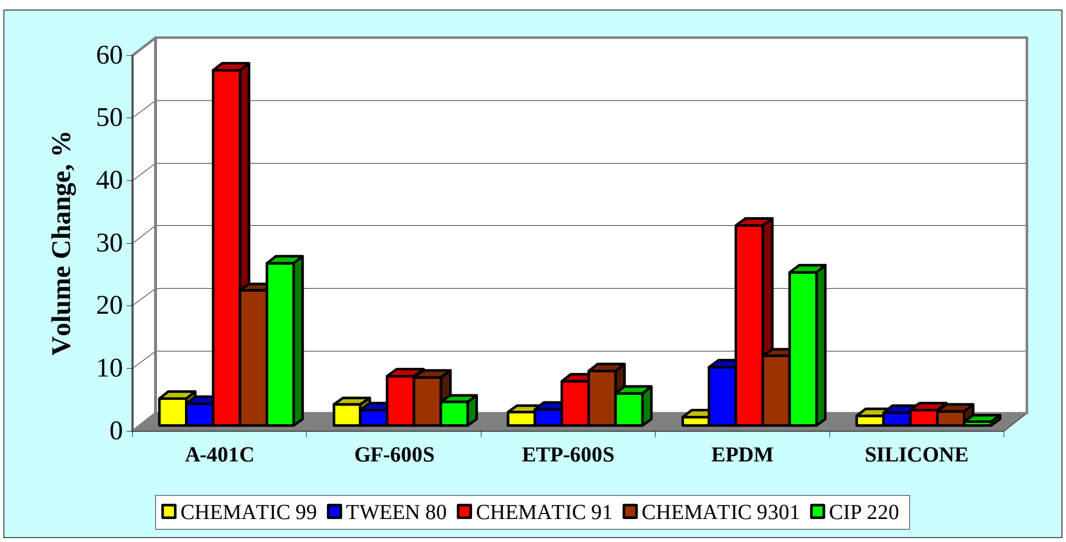
Figure 4
Volume Change* for Viton® GF-600S and Viton® ETP-600S versus Viton® A-401C
After 1008 Hours @ 100°C in Cleaning Fluids



ASTM D471: V.I. = Volume Increase

In addition to providing superior resistance to a wider variety of cleaning fluids than a bisphenol-cure dipolymer FKM, Viton® GF-600S and Viton® ETP-600S are also superior in this regard to seals made with EPDM. Figure 5 compares the volume change for Viton® GF-600S and Viton® ETP-600S compared to a commercially available EPDM material, after a 1008 hour exposure to various cleaning fluids, and, as indicated in this chart, these two fluoroelastomers exhibit lower changes in volume than the EPDM in all the cleaning fluids tested.

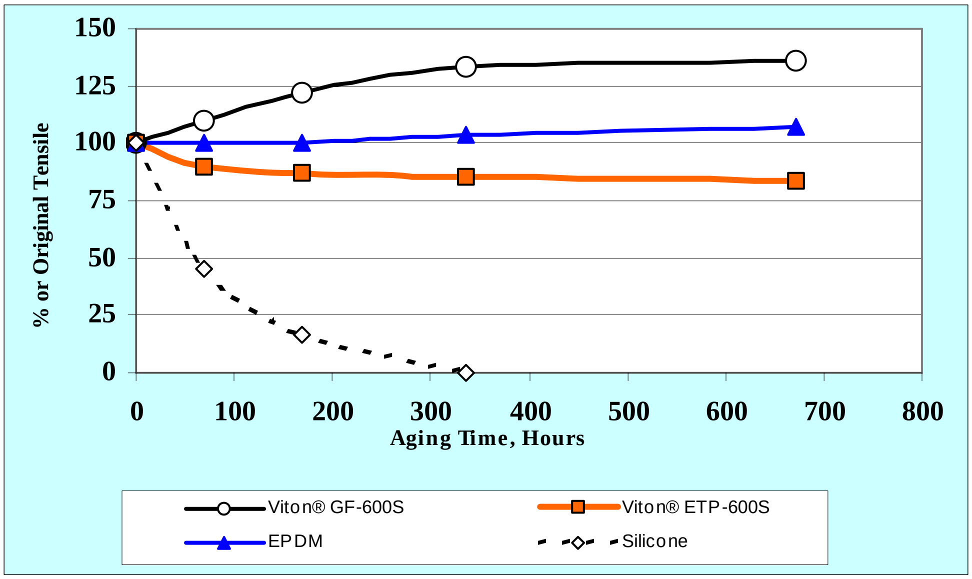
Figure 5
Volume Change* for Viton® versus EPDM and Silicone
After 1008 Hours @ 100°C in Cleaning Fluids



ASTM D471: V.I. = Volume Increase

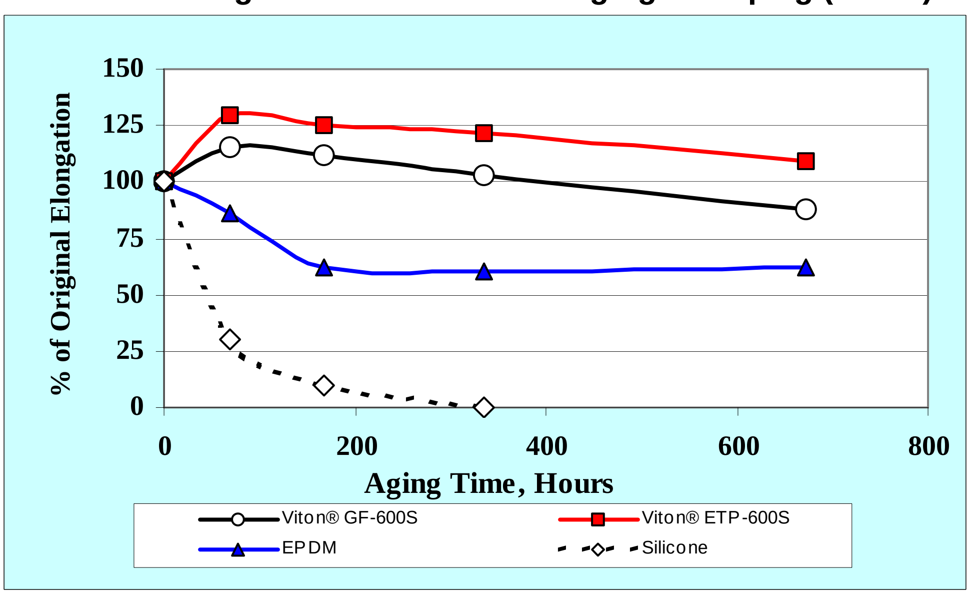
Note that, like the two peroxide-cured types of Viton®, a sample of a commercially available, platinum-cured silicone, also exhibited small (<10%) changes in all the cleaning fluids tested, indicating that this material would provide acceptable service in these fluids. However, steam often is used in combination with process cleaning fluids, and this must be taken into account when choosing a sealing material. Although platinum-cured silicone exhibits good resistance to a wide variety of cleaning fluids, it does not typically provide good serviceability in steam environments.

Figure 6
% Retention of Tensile Strength* After Aging in 80 psig (156°C) Steam



*ASTM D471

Figure 7
% Retention of Elongation*At Break After Aging in 80 psig (156°C) Steam



*ASTM D471

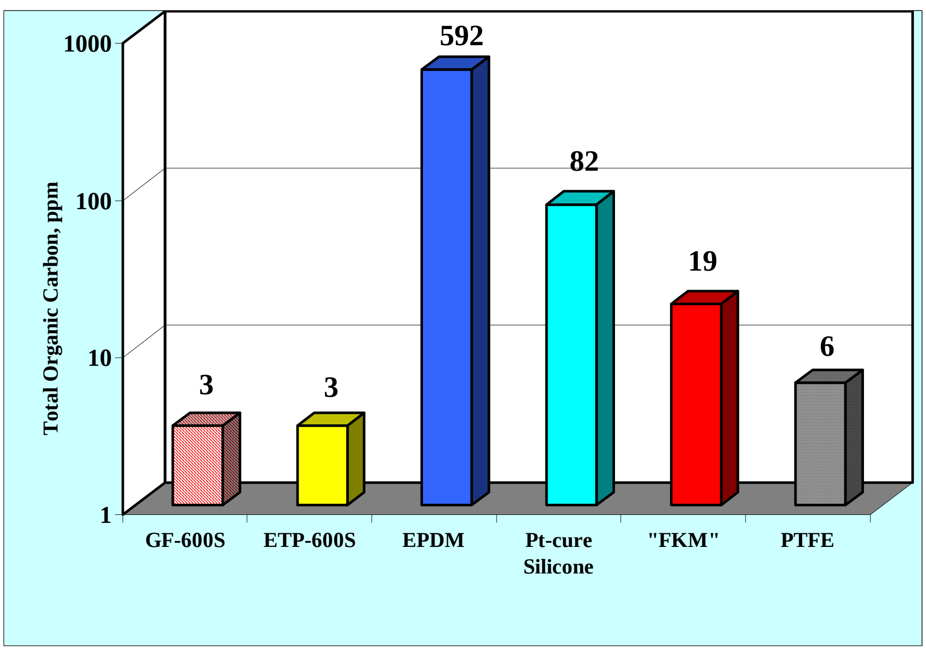
As shown in Figures 6 and 7, the samples of platinum-cured silicone rubber were completely degraded after being exposed to 80psi steam (156°C) steam for 336 hours, losing 100% of their original tensile strength and elongation.

Extractable Carbon, Metal

In addition to providing good sealing capability, and the resistance to process and cleaning fluids that is needed to maintain sealing integrity, exhibiting low levels of extractable materials is also of significant value to food and pharmaceutical applications. Excessively high levels of extractable organic or metallic materials from an elastomer could potentially contaminate a process stream, and/or affect the flavor of a food.

Modern, bisphenol-cure fluoroelastomers typically exhibit relatively low levels of extractible carbon, particularly in the case of seals that have been oven postcured, in addition to the press cure that is required for vulcanization. Oven postcure cycles for fluoroelastomer parts typically range between 200°C to 250°C, and this post-treatment of molded parts serves to drive off most carbon-based materials (unused curative, process aids, etc.) that might remain in a molded seal that has not been postcured. Compared to other elastomers, postcured fluoroelastomers have low levels of extractable organic carbon, as indicated by the data in Figure 8.

Figure 8
Total Organic Carbon*: Viton® GF-600S and Viton® ETP-600S Versus Other Sealing Materials

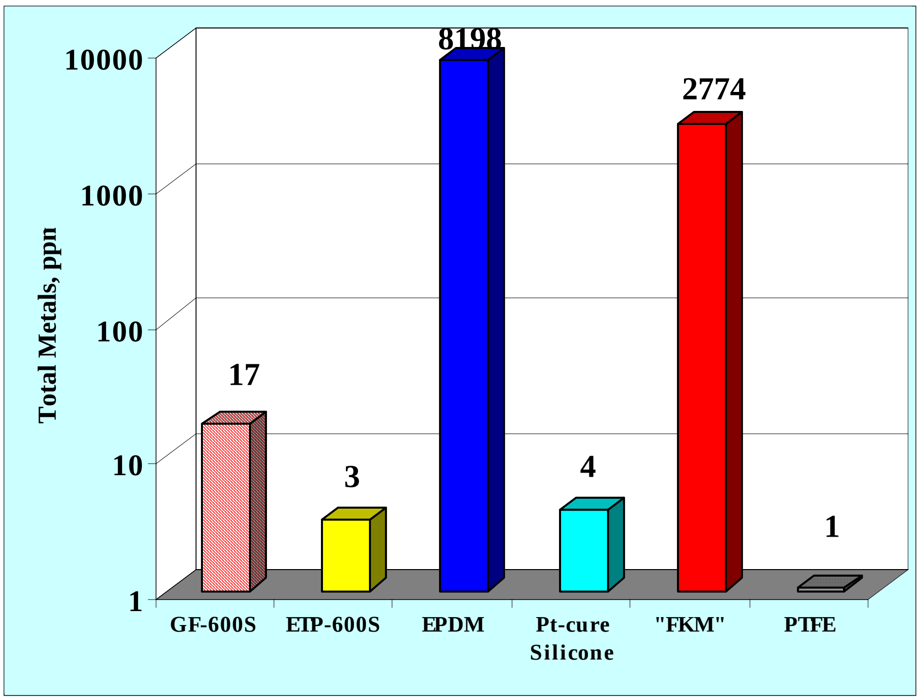


*EPA Method 415.1

Note that the y-axis of the chart in Figure 8 is a logarithmic scale, and that the level of total extracted carbon for the samples made with Viton® GF-600S and Viton® ETP-600S are approximately 1/200th that of the EPDM sample, less than 1/20th that of the platinum-cure silicone sample, and less than a 1/6th that of a bisphenol-cure dipolymer FKM. Worthy of note, too, is the fact that, with regard to total extractible carbon, the samples made with Viton® GF-600S and Viton® ETP-600S are about the same (3 vs 6ppm) as that of the PTFE sample.

Important differences in extractible metals are also seen, between Viton® GF-600S and Viton® ETP-600S and other Sealing Materials. The results of a 5% nitric acid extraction are illustrated in Figure 9, and show that the peroxide cure types of Viton can be formulated so that levels of extractible metals are significantly lower than in conventional, bisphenol-cure dipolymer FKM, EPDM or silicone formulations.

Figure 9
Extractible Metals*: Viton® GF-600S and Viton® ETP-600S Versus Other Sealing Materials

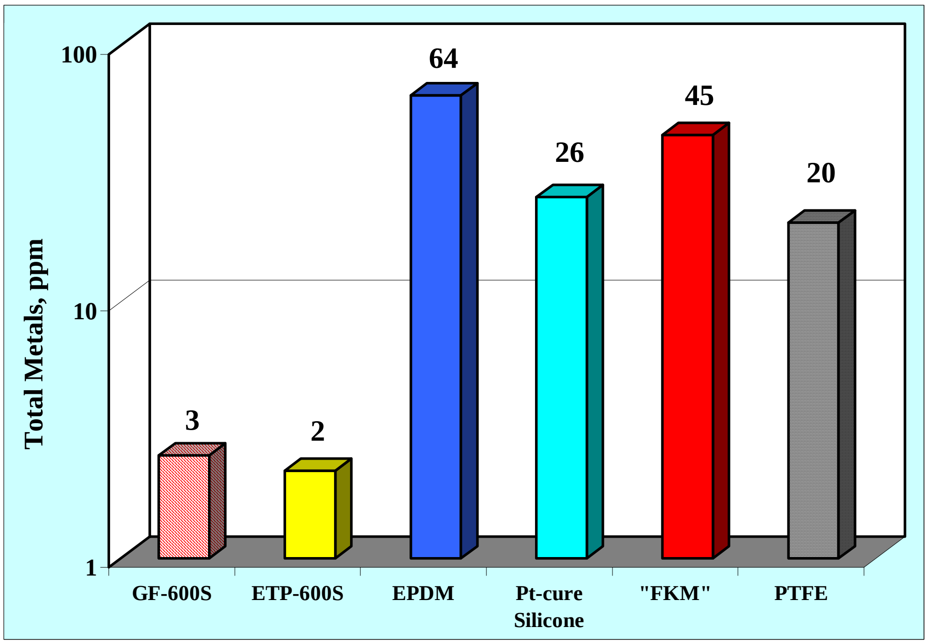


*EPA Method 6010A – 5% Nitric Acid

The level of metals (17ppm) for the sample containing Viton® GF-600S is about 0.2% of the level of metals extracted from the EPDM sample, and approximately 0.6% of the level extracted from the bisphenol-cure, dipolymer FKM. Both samples based on Viton® GF-600S and Viton® ETP-600S were, as in the case of total organic carbon, on a level similar to that of the PTFE material that was tested.

The same test, conducted in WFI, exhibited similar degrees of difference between the samples. As shown in figure 10, samples based on Viton® GF-600S and Viton® ETP-600S exhibited levels of metals extracted in WFI that were approximately 5%, 12%, and 7%, respectively, of the levels of the samples made with EPDM, silicone, and the conventional, bisphenol-cure dipolymer FKM, and about 15% of the level of that exhibited by the PTFE sample.

Figure 10
Extractible Metals*: Viton® GF-600S and Viton® ETP-600S Versus Other Sealing Materials



*EPA Method 6010A – WFI

Compression Set Resistance

Fluoroelastomers are well known, not only for their excellent resistance to heat and fluids, but also for the excellent resistance to creep and compression set. Modern fluoroelastomers, in general, provide significantly better, long-term sealing capability than other elastomers, as indicated by resistance to compression set. Compression set is a measure of the degree to which a sample, aged under constant deformation (25% deflection, for ASTM D395, Method "B") will regain its original height, when released. Low values of compression set are indicative of a good retention of sealing force. Conversely, high values of compression set indicate that the material has lost its ability to maintain a seal.

PTFE is a thermoplastic, and, unlike crosslinked elastomers, like FKM, EPDM, and silicone, the polymer chains are not linked together. Thus, when placed under a load, seals made with PTFE will deform, or "creep", and will lose their ability to maintain a seal. In order to maintain a seal using PTFE, mechanical "assistance" must be provided. Without some form of mechanical "assistance" that can maintain a constant load on the seal (e.g., spring loading), periodic retightening of the clamps holding the PTFE seals will be required.

Summary

In summary, vulcanizates made with the high-fluorine content, peroxide-cure Viton® GF-600S provide a superior combination of the following characteristics, compared to other, bisphenol-cure fluoroelastomers, and compared to EPDM and platinum-cure silicone:

- Very good resistance to steam and caustic solutions
- Very good resistance to a wide variety of commercial process cleaning solutions
- Excellent resistance to a wide variety of process chemicals & fluids
- Can be formulated to provide levels of extractible carbon similar to that of PTFE
- Can be formulated to provide levels of extractible metals similar to that of PTFE

In addition to providing the same combination of physical property characteristics listed above, vulcanizates made with Viton® ETP-600S also exhibit resistance to chemicals and fluids to which other fluoroelastomers, including GF-600S, are not resistant, such as low molecular weight ketones, aldehydes, esters, and ethers.

The physical property characteristics for Viton® GF-600S and Viton® ETP-600S, compared to a bisphenol-cure, dipolymer FKM (Viton® A-401C) and compared to platinum cure silicone and EPDM are summarized below, in Table IV.

Table IV
Physical Property Characteristics of Viton® GF-600S and Viton® ETP-600S Compared to Other Sealing Materials

Sealing Material	Resistance to Compression Set	Resistance to Steam	Resistance to Commercial Cleaning Solutions	Resistance to a Broad Variety of Types of Chemicals, Fluids	Levels of Extractible Carbon	Levels of Extractible Metals
Viton® A-401C	◎	△	△	△	△	△
Viton® GF-600S	◎	◎	◎	◎	◎	◎
Viton® ETP-600S	◎	◎	◎	◎	◎	◎
EPDM	△	◎	△	●	●	●
Pt-cure Silicone	△	●	◎	●	●	●
PFTE	●	◎	◎	◎	◎	◎

◎ = Best △ = Good ● = Worst