

New Peroxide Curable Advanced Polymer Architecture Viton® for Plate Heat Exchanger Gasket (PHEG) Applications

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Abstract

Plate heat exchangers are used in the industrial / energy production market segment and present a difficult sealing problem that can often only be resolved using fluoroelastomer seals. Viton® GBL and GF types are typically used to fulfill this arduous application. Heat exchangers are often built from multiple layers of titanium plates which permit the transfer of heat via a complex system of channels through which hot fluids flow. The multiple plates are sealed using gaskets of Viton® which can be very large in terms of volume and length. The sealed area of a titanium plate can be in the region of one metre (length) by half a metre (width) indicating the outside dimensions of the gasket. Gasket thicknesses vary but might typically be in the 6 to 12 mm region. A complex series of internal channels requires additional sealing functionality.

The fluid streams which must be sealed in the case of industrial heat exchangers include a mixture of hot water and steam at high pressure as well as hot acidic media. Due to the high pressures involved the hot chemical streams can be at temperatures in the region of 160°C. New designs are expected to operate in the 180°C to 200°C temperature range.

There are several problems associated with the use of fluoroelastomers in such applications. One of the most perplexing problems is that of corrosion of the titanium heat exchanger plates which are very expensive to replace. It is thought that the corrosion comes from HF evolution as a result of very high temperature service conditions. Other difficulties are associated with how to compound the fluoroelastomer to give good long term sealing integrity in the face of hostile service conditions which usually requires the use of lead oxide stabilized formulations. Last but not least are the manufacturing difficulties associated with the fabrication of such large and complex components.

This paper describes how new materials made with Advanced Polymer Architecture Viton® offer excellent resistance to the relevant chemical media and can be compounded to give a lower level titanium corrosion without compromising other functional properties. These functional benefits are also accompanied by improvements in mould flow, cure rate and demoulding performance, offering the ability to more economically manufacture high quality, gaskets.

Polymer Property and Processability Considerations for PHEG Applications

The critical end use properties are;

- original physical properties indicative of resistance to crushing and groove extrusion forces
- long term compression set resistance and compression stress relaxation
- heat resistance
- resistance to hot water and steam
- resistance to aqueous streams containing sulfuric acid

Polymers like Viton® GF or Viton® GBL-900 have typically been used in the past due to their excellent acid and heat resistance as well as resistance to aqueous media. A properly formulated, compound can give quite low compression set and provide the balance of tensile strength, modulus and elongation at break that are necessary for good sealing performance. Polymers like Viton® GBL-900 are sometimes chosen for their improved performance at lower temperatures and are preferentially selected for hot water resistance whilst GF types are preferentially selected for those applications which require resistance to strong acids.

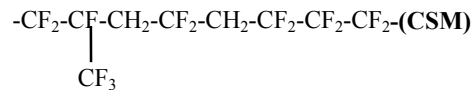
In addition to the functional requirements, good performance in all aspects of processability are required to economically make high quality gaskets. Some of the processability requirements are :

- consistent extrusion of compression moulding pre-form cord
- flow properties for easy mould filling
- fast curing for optimal cycle times
- easy demoulding with low mould sticking (and low mould fouling)

In order to achieve the required balance of compression set resistance and fluid resistance properties using Viton® GF or GBL, it is necessary to use lead oxide as an acid acceptor. Apart from being ecologically undesirable it is well known that lead oxide provokes processing problems (mould sticking and fouling) and recent tests indicate that lead oxide also promotes sticking of vulcanized gaskets to titanium plates which are used in plate heat exchangers.

Viton® GF and GBL Compositions

Both Viton® GF and Viton® GBL types are terpolymers of vinylidene fluoride (VF₂), hexafluoropropylene (HFP) and tetrafluoroethylene (TFE) with a cure site monomer (CSM) to facilitate curing using an organic peroxide / coagent system. They have the basic structure as follows :



and differ mainly in the monomer levels which are selected to give the GF polymer a fluorine content approaching 70% and the GBL polymer a fluorine content of around 68%. The higher fluorine level of Viton® GF is designed to provide optimal fluid resistance. The GF composition was first introduced in 1980 by Bauerle & Finlay (1) and the GBL composition was first introduced by Tabb & Stevens (2) in 1985.

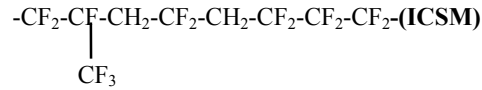
DuPont Dow Elastomers has recently developed and introduced new polymerization and curing technology which has allowed the end use properties and processability of specialty fluoroelastomers like Viton® GF and Viton® GBL types to be significantly improved. For the purposes of this paper the new products are referred to by their experimental codes as follows :

VTX-8600 is a new version of the Viton® GF family of polymers

VTX-8650 is a new version of the Viton® GBL family of polymers

VTX-8600 and VTX-8650 have a similar composition to Viton® GF and GBL, respectively, in terms of monomer levels but are widely different in terms of molecular structure, branching and contain a new cure site monomer. It is these subtle differences in structure and the new

cure site monomer that bring the huge improvements in processability and properties. The new compositions have the following basic structure :



where ICSM represents the new cure site monomer. These new polymers were first introduced by Stevens and Lyons in 2001 (3).

Processing Characteristics - Flow

Heat exchanger gaskets are predominantly manufactured by compression moulding using lengths of extruded strip as pre-forms. Ease of flow is important in the case of both pre-form preparation and mould filling. Pre-forms are usually prepared via a piston extrusion process and the quality of moulded gaskets can be strongly influenced by the surface quality and dimensional stability of the extruded pre-form. Polymer structure, such as molecular weight distribution, chain branching as well as chain termination chemistry play an important role in flow behavior and determine to a large extent the quality of the extrudate. The pressure required to extrude compound through a die is related to the combination of shear and extensional stresses generated in the compound under flow. One feature of the new polymers is that for a given Mooney viscosity they generate much lower levels of both shear and extensional stress during flow than many other fluoroelastomers. Figures 1 and 2 are generated from capillary rheometer test data and show how the new GF polymer gives lower shear and elongational stresses even though it has a higher Mooney viscosity. Low stress generation under flow results in easier extrusion, which is certainly an advantage, but also lower die swell – ultimately one would expect more precise pre-form dimensional control. In addition due to the lower level of stored internal stresses one would expect better stability of pre-form dimensions with time. It should be noted that the flow properties of the new GBL family of polymers are equally improved.

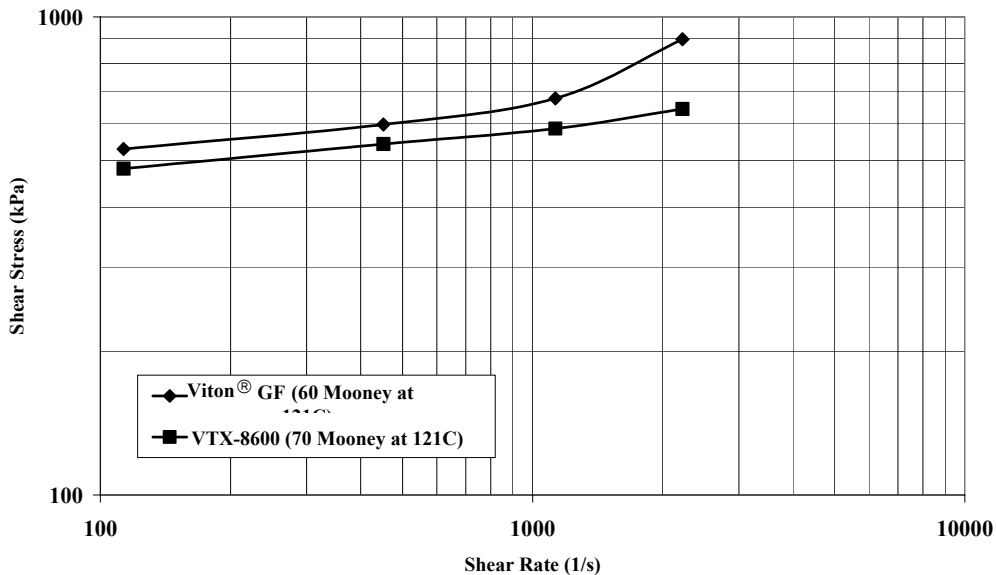


Figure 1. Shear Stress vs. Shear Rate for Viton® GF Family Polymers

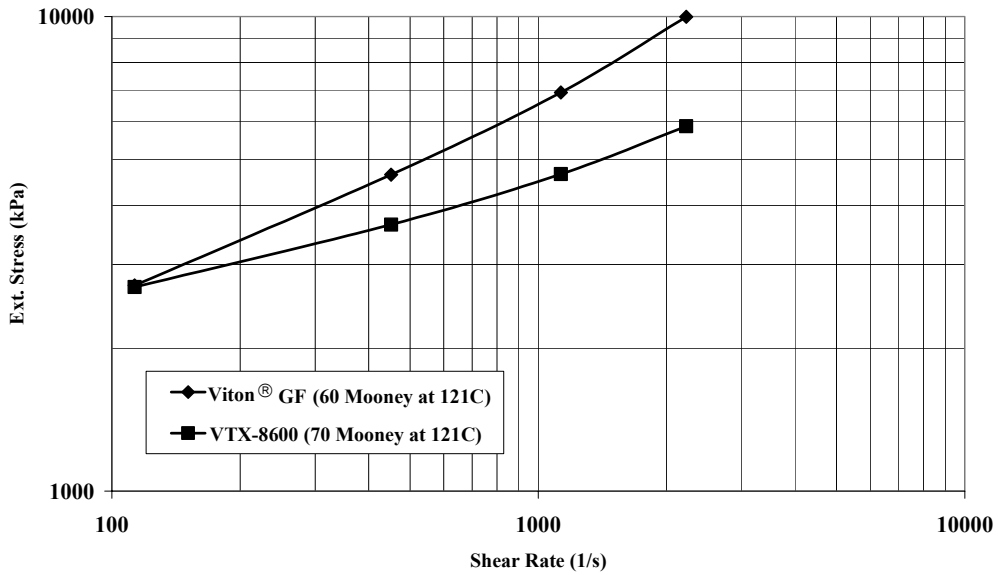


Figure 2. Elongational Stress vs. Shear Rate for Viton® GF Family Polymers

Processing Characteristics - Curing

Another important aspect of processability is curing. The new generation polymers contain a new cure site monomer which provides a more efficient curing process using conventional organic peroxides and coagents. The best way to illustrate this improvement in curing efficiency is to compare the MDR curves for two compounds as in Figure 3 below. The compounds contain 100 phr polymer, 30 phr MT carbon black, 3 phr zinc oxide, 3 phr triallylisocyanurate and peroxide levels as shown (45% active 2,5-dimethyl 2,5-bis [t-butyl peroxy] hexane on inert filler).

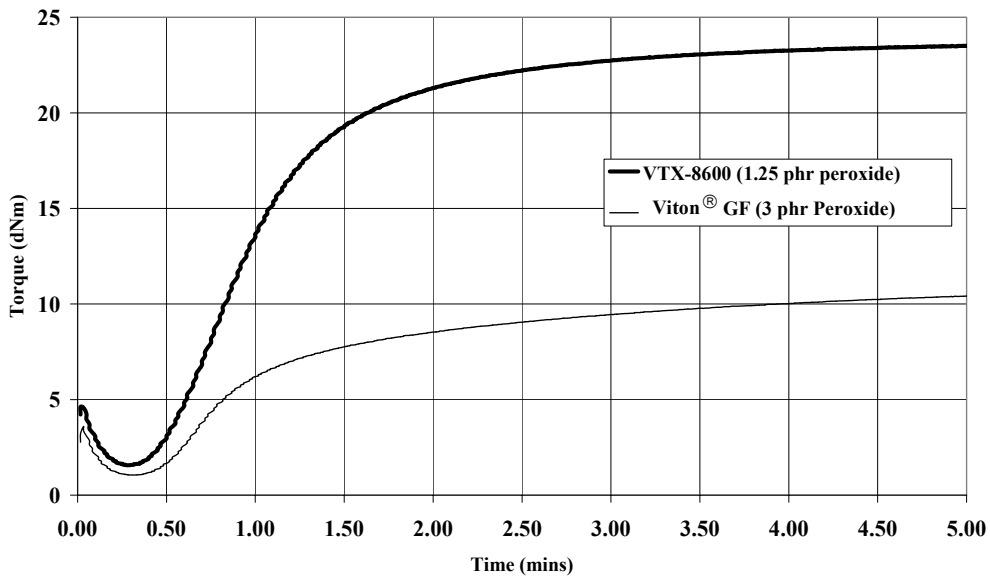


Figure 3. MDR @ 180°C for Viton® GF Family Polymers (0.5° arc , 5 mins)

As indicated the VTX-8600 compound cures significantly faster and to a higher state of cure even though it contains only 1.25 phr peroxide vs. 3 phr peroxide for the compound based on Viton® GF. The improved curing efficiency is mainly due to the new cure site monomer employed in VTX-8600 but also to the chain end configuration of the new polymer, which also favours more efficient curing.

The implications are that VTX-8600 will provide shorter curing cycles and a higher state of cure. The benefits of this improved cross-link network will become evident later during a discussion of the physical properties and compression set resistance of vulcanized test pieces. Once again, the same trend is true for the GBL family of polymers.

Processing Characteristics – Demoulding Performance

Moulded parts will always offer some resistance to being de-moulded and the material has to withstand any stresses induced during this operation to avoid defects. In the case of geometrically simple parts like gaskets the resistance to de-moulding comes almost entirely from the tendency of the material to stick to the mould surface since there is little deformation involved. To assess the mould release of the new polymers tests, have been performed in compression moulding using a specially designed mould and test protocol. An O-ring tool was fabricated using current industry design, methods and materials with cavities dimensioned to give a large surface area to deliberately make de-moulding more difficult. De-moulding was effected using a specially designed air line so that no physical contact could occur between the air line nozzle and the O-rings – the only de-moulding force came directly from the air blast. The mould consisted of 120 cavities arranged in two sets of 60 to allow simultaneous evaluation of control and experimental materials under identical processing conditions. A further feature of the test mould is that it was designed to self de-flash in the sense that the O-rings are automatically separated from excess flash. This ensures that release of the O-rings is not assisted by the flash (see Figure 4 below).

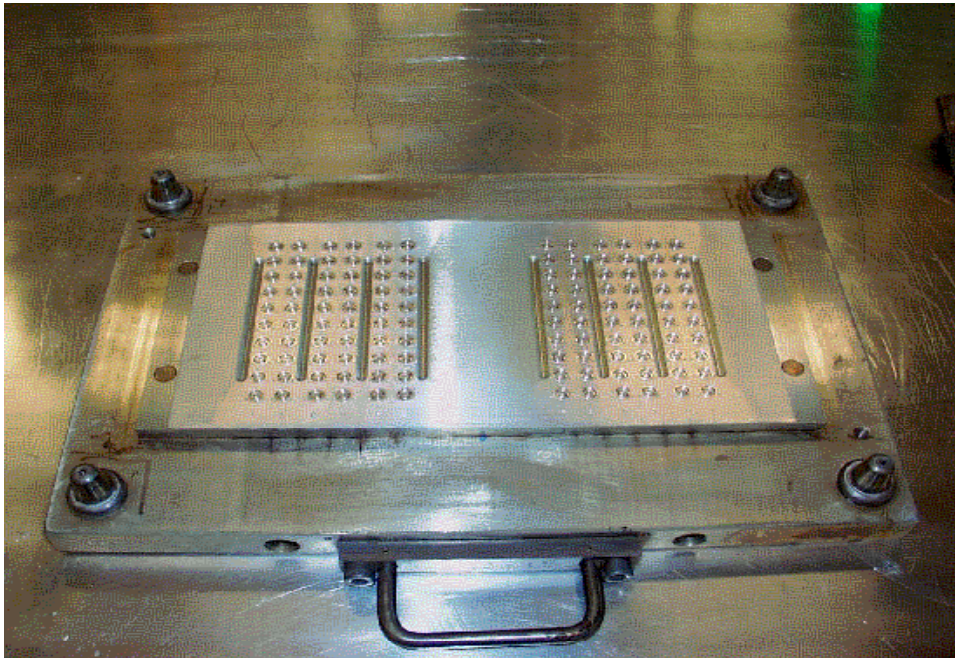


Figure 4. Test Mould Used for Demoulding Evaluations

The following procedure was used to evaluate demoulding performance:

1. Clean each cavity using a small rotary brass wire brush
2. Clean the total flat surface using a brass wire brush
3. Completely wash the mould surface, including cavities, with solvent (acetone was used)
4. Assemble mould in the press and heat to desired moulding temperature
5. Apply semi-permanent mould release agent to both upper and lower mould surfaces
6. Load mould with extruded cord using a loading frame to position the cord directly over the cavities to ensure equal flow and cure time for each cavity (experimental material on one side and control material on the other)
7. Close mould and cure for the selected time
8. Demould O-rings using only air pressure and record those which remained stuck
9. Repeat steps 6 through 8 until around fifty (50) moulding cycles are complete (50 moulding cycles was previously determined to be sufficient to distinguish demoulding performance between materials)

The results of a test are presented as a plot of the percentage of sticking cavities per moulding cycle for the duration of the moulding trial. The reason for using a mould release agent was primarily to improve the performance of the control compound since if the control compound takes too long to de-mould, the performance of the other material under test can be impaired. The test data obtained are shown in Figure 5 for a comparison between Viton® GF and VTX-8600. The compounds contain 100 phr polymer, 30 phr MT carbon black, 3 phr zinc oxide, 3 phr triallylisocyanurate, 3 phr organic peroxide (45% active 2,5-dimethyl 2,5-bis [t-butyl peroxy] hexane on inert filler), 0.5 phr Octadecylamine and 1 phr Viton® Process Aid #2.

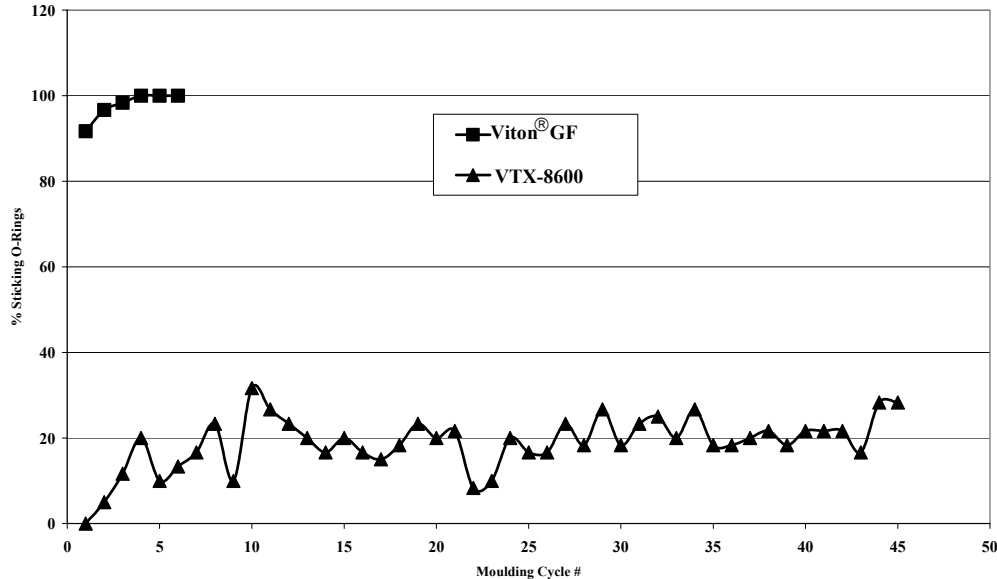


Figure 5. Demoulding Test Data – Viton® GF vs. VTX-8600

The data presented in Figure 5 clearly illustrates the advantage of the new VTX-8600 over Viton® GF in terms of mould sticking tendency. In this test the average sticking rate for VTX-8600 was 19% vs. 97% for Viton® GF. It should be noted that the sticking rings are those which could not be removed using air pressure alone and in many cases they could be successfully removed by hand. This is a very arduous test and the data presented are only

intended to illustrate the reduced sticking tendency of the new technology polymer. Test data for the GBL type polymers show a similar improvement for VTX-8650 vs. Viton® GBL-900.

Physical Properties for End Use Performance

The properties of the GF and GBL family polymers are compared in the following tables.

<i>Polymer Base</i>	<i>Viton® GBL-900</i>	<i>VTX-8650</i>	<i>Viton® GF</i>	<i>VTX-8600</i>
Viton® GBL-900	100			
VTX-8650		100		
Viton® GF			100	
VTX-8600				100
Zinc Oxide	3	3	3	3
MT Carbon Black	30	30	30	30
Trimethylisocyanurate	3	3	3	3
45% organic peroxide*	3	3	3	3

Table 1. Compound Recipes

* (45% active 2,5-dimethyl 2,5-bis [t-butyl peroxy] hexane on inert filler)

<i>Polymer Base</i>	<i>Viton® GBL-900</i>	<i>VTX-8650</i>	<i>Viton® GF</i>	<i>VTX-8600</i>
M-L (dNm)	2.8	2.1	2.1	2.4
ts-2 (min)	0.6	0.4	0.6	0.4
t'50 (min)	1.1	0.6	1.0	0.6
t'90 (min)	3.3	0.9	3.3	0.9
t'95 (min)	4.2	1.2	4.2	1.2
M-H (dNm)	18.8	28.0	14.1	30.5

Table 2. MDR @ 177°C, 0.5° arc, 6 mins

<i>Polymer Base</i>	<i>Viton® GBL-900</i>	<i>VTX-8650</i>	<i>Viton® GF</i>	<i>VTX-8600</i>
Minimum, MU	49	33	44	36
2 Pt. Rise (min)	15.9	16.4	13.9	12.7
5 Pt. Rise (min)	18.7	18.0	16.3	13.5
10 Pt. Rise (min)	21.6	19.4	20.3	14.2

Table 3. Mooney Scorch @ 121°C

<i>Polymer Base</i>	<i>Viton® GBL-900</i>	<i>VTX-8650</i>	<i>Viton® GF</i>	<i>VTX-8600</i>
<i>Post Cure Time</i>	<i>16hrs</i>	<i>16hrs</i>	<i>16hrs</i>	<i>2hrs</i>
100% Modulus, MPa	7.3	4.2	6.6	5.7
Tensile Strength, MPa	20.9	20.5	20.8	20.1
Elongation @ Break, %	174	301	228	269
Hardness, A, pts	73	73	74	73

Table 4. Physical Properties Measured @ 23°C, Post Cured at 232°C as indicated

A characteristic of the new polymers is that they tend to give significantly higher elongation at break for a given compound hardness and tensile strength. In Table 4 the compound based on VTX-8600 is post cured for only 2 hrs to illustrate the low post cure capability imparted by the new technology.

It is also true that the new polymers also have better properties when measured at high temperature in the non post cured state and data is presented in Table 5 to illustrate this for the GBL family of polymers.

<i>Polymer Base</i>	<i>Viton® GBL-900</i>	<i>VTX-8650</i>
<i>Post Cure Time</i>	<i>None</i>	<i>None</i>
10% Modulus, MPa	0.42	0.64
50% Modulus, MPa	1.47	1.96
Tensile Strength, MPa	3.43	4.62
Elongation @ Break, %	102	133

Table 5. Physical Properties Measured @ 150°C, Not Post Cured

The physical properties at high temperature are important at the demoulding stage and the combination of better strength at demoulding temperatures with a generally much lower tendency for mould sticking should provide a more robust gasket manufacturing process.

Compression set resistance is very important in static sealing applications and the new polymers provide a significant improvement in this area as indicated in Table 6.

<i>Polymer Base</i>	<i>Viton® GBL-900</i>	<i>VTX-8650</i>	<i>Viton® GF</i>	<i>VTX-8600</i>
<i>Post Cure @ 232°C</i>	<i>16hrs</i>	<i>16hrs</i>	<i>16hrs</i>	<i>2hrs</i>
22 hrs @ 200°C	14	15	24	14
336 hrs @ 200°C	39	30	53	29
	<i>No Post Cure</i>	<i>No Post Cure</i>	<i>No Post Cure</i>	<i>No Post Cure</i>
22 hrs @ 200°C	21	12	30	14
336 hrs @ 200°C	54	25	66	38

Table 6. Compression Set Resistance, Plied Discs, Post Cured as indicated

The data in Table 6 illustrate the excellent compression set resistance of the new polymers either with or without a post cure cycle. The data also illustrate that only a short post cure is required in the case of VTX-8650 and VTX-8600.

The low compression set values imply improved long term sealing integrity and this can be backed up by long term stress relaxation data at high temperature. Stress relaxation data are presented in Figure 6 for the GBL family of polymers. These data were measured at 150°C using a Wallace Shawbury Stress Relaxometer (Mk III) and provide even more convincing evidence of the better long term sealing integrity expected from the new technology polymers like VTX-8650 and VTX-8600.

The combination of physical properties, compression set resistance and seal force retention shown by the data presented indicate the new compositions would make excellent heat exchanger gasket materials. The high tensile strength and elongation at break should give good extrusion resistance, especially if compounded to give a higher modulus by using more

reinforcing fillers. Other tests, not reported here, have shown that the 100% modulus can be raised significantly without significant impact on elongation at break.

Wallace Shawbury Stress Relaxometer Data for GBL Family Polymers

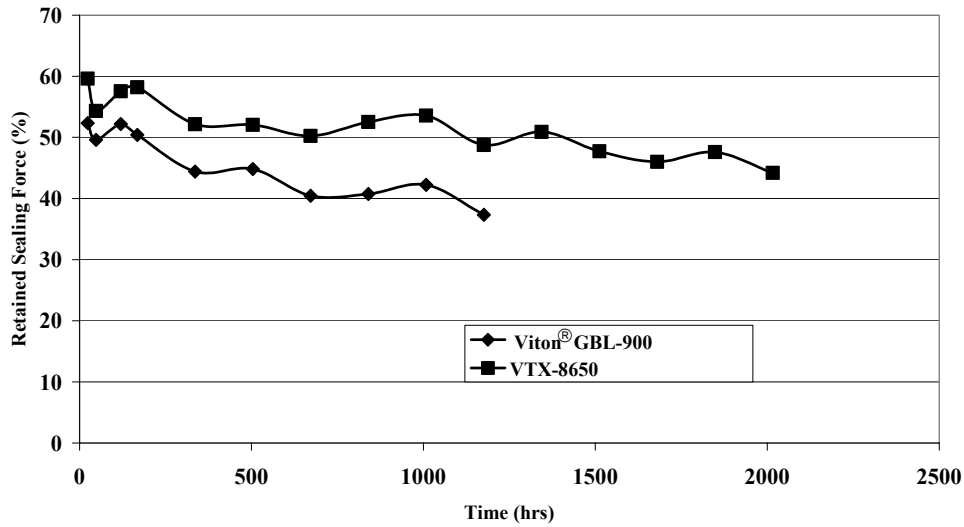


Figure 6. Retained Sealing Force vs. Time for GBL Family Polymers (tested at 150°C in air)

Heat Resistance

Heat resistance is also important for high temperature heat exchanger applications. Polymers exhibiting good heat resistance would be expected to give longer seal life at high temperature. In developing the new polymer structure and cure site monomer is it has been possible to achieve better processing and physical properties already reported without negatively impacting heat resistance. Hot air aging data at 250°C and 275°C are presented in tables 7 and 8 for the GF and GBL families of polymer. Note that the new technology polymers are given a short post cure of just 2 hrs @ 232°C in each case.

<i>Polymer Base</i>	<i>Viton® GBL-900</i>	<i>VTX-8650</i>	<i>Viton® GF</i>	<i>VTX-8600</i>
<i>Post Cure Time</i>	<i>16hrs</i>	<i>2hrs</i>	<i>16hrs</i>	<i>2hrs</i>
100% Modulus, MPa	8.1	3.7	6.7	5.5
(% Change, M-100)	10.4	-8.4	1.4	-3.5
Tensile Strength, MPa	19.1	20.2	21.91	20.7
(% Change, TS)	-8.4	3.4	5.4	2.8
Elongation @ Break, %	168.0	352.3	242.7	272
(% Change, EB)	-3.6	14.7	6.6	1
Hardness, A,pts	73	71	74	75
(Pts Change)	0	2	0	2

Table 7. Physical Properties Measured @ 23°C, Post Cured at 232°C as indicated Heat Aged 70hrs @ 250°C

<i>Polymer Base</i>	<i>Viton® GBL-900</i>	<i>VTX-8650</i>	<i>Viton® GF</i>	<i>VTX-8600</i>
<i>Post Cure Time</i>	<i>16hrs</i>	<i>2hrs</i>	<i>16hrs</i>	<i>2hrs</i>
100% Modulus, MPa	6.6	3.3	4.0	3.2
(% Change,M-100)	-10.5	-19.2	-39.1	-43.8
Tensile Strength, MPa	14.5	13.0	13.2	10.0
(% Change,TS)	-30.5	-33.6	-36.5	-50.3
Elongation @ Break, %	180.0	321.4	321.4	371.5
(% Change,EB)	3.3	4.7	41.2	38.0
Hardness, A,pts	74	70	72	75
(Pts Change)	1	1	-2	2

Table 8. Physical Properties Measured @ 23°C, Post Cured at 232°C as indicated Heat Aged 70hrs @ 275°C

The heat resistance data presented indicates polymers that have good thermal stability. It should be noted that there is significant scope for improving the heat resistance of seals via selective choice of peroxide level - high levels of peroxide are known to be detrimental to heat resistance. As has already been illustrated the new polymers cure well with only low levels of peroxide.

Fluid Resistance

Good resistance to the relevant fluids is important for high temperature heat exchanger applications. Data is presented here to compare the GF and GBL families of polymer. As already mentioned hot water resistance is important for both GBL and GF type applications whilst GF types are generally selected for their better resistance to acids.

Table 9 compares the acid resistance of Viton® GF to VTX-8600

<i>Polymer Base</i>	<i>Viton® GF</i>	<i>VTX-8600</i>	<i>Viton® GF</i>	<i>VTX-8600</i>
<i>Post Cure Time</i>	<i>16hrs</i>	<i>2hrs</i>	<i>16hrs</i>	<i>2hrs</i>
<i>Chemical Media</i>	<i>Nitric Acid</i>	<i>Nitric Acid</i>	<i>96% Sulfuric Acid</i>	<i>96% Sulfuric Acid</i>
Tensile Strength, MPa	10.67	10.4	24.71	21.18
(% Change,TS)	-48.7%	-48.3%	18.9%	5.3%
Elongation @ Break, %	370	352	209	210
(% Change,EB)	62.5%	30.8%	-8.3%	-22.2%
Hardness, A,pts	49	53	76	75
(Pts Change)	-25	-20	2	2
Volume Change (%)	31.2	23.4	2.8	2.8

Table 9. Physical Properties Measured @ 23°C, Post Cured at 232°C as indicated Aged 168hrs @ 70°C in Chemical Media indicated

The data show excellent retention of tensile strength and elongation at break for VTX-8600 but most striking is the low volume swell in hot concentrated nitric acid for the new polymer which can be expected to provide advantages in applications such heat exchanger gaskets.

The other type of chemical stream which heat exchanger gaskets must resist is hot water. One of the characteristics of the new polymers is that they are inherently more resistant to hot water as illustrated by the data in Table 10 which compares the hot water resistance of both

GBL and GF families of polymer. Note that the data are for compounds containing 3 phr zinc oxide and as such they are not optimized for water resistance.

Polymer Base	Viton® GBL-900	VTX-8650	Viton® GF	VTX-8600
Post Cure Time	16hrs	2hrs	16hrs	2hrs
Tensile Strength, MPa	18.7	18.3	17.6	18.6
(% Change, TS)	-10.5%	-3.3%	-15.6%	-7.4%
Elongation @ Break, %	202	393	278	294
(% Change, EB)	15.9%	12.3%	22.3%	9.4%
Hardness, A,pts	68	71	72	73
(Pts Change)	-5	-1	-2	0
Volume Change (%)	8.9	3.2	6.2	4.5

Table 10. Physical Properties Measured @ 23°C, Post Cured at 232°C as indicated Aged 168hrs @ 100°C in water

The data in Table 10 clearly illustrates the low water swell of the new technology polymers as well as good retention of physical properties. For a given recipe VTX-8650 and VTX-8600 will generally give around half the volume swell of Viton® GBL-900 and Viton® GF in this type of test. The exception is when lead oxide is used as an acid acceptor where all compounds would give volume swells in the region of 0.5 to 1%.

The water swell of compounds based on VTX-8600 and VTX-8650 can be further reduced to around 2 to 2.5% by elimination of the metal oxide altogether. This is not possible using Viton® GF or Viton® GBL-900 since for these polymers a metal oxide is required to neutralize residual chain end acidity and permit efficient curing. Most metal oxides form soluble metal fluorides during vulcanization and this can have quite a dramatic impact on water swell as illustrated in Table 11 using Viton® GBL-900 based recipes.

Metal Oxide	ZnO	PbO	MgO	Ca(OH)₂	CaO
Viton® GBL-900	100	100	100	100	100
Zinc Oxide	3	-	-	-	-
70% PbO Masterbatch	-	3.3	-	-	-
Low Activity MgO	-	-	3	-	-
Calcium Hydroxide	-	-	-	3	-
Calcium Oxide	-	-	-	-	3
MT Carbon Black	30	30	30	30	30
Trimethallylisocyanurate	2	2	2	2	2
45% organic peroxide*	4	4	4	4	4
Hot Water Aged - 168 hrs @ 100 °C					
Volume Swell, %	9	2	9	10	12
Compression Set 70 hrs @ 200 °C					
Compression Set, % (O-Rings)	53	35	53	36	49

Table 11. Influence of metal oxide on Water Swell and Compression Set Resistance

*(45% active 2,5-dimethyl 2,5-bis [t-butyl peroxy] hexane on inert filler)

Metal oxide selection is also important for compression set resistance and resistance to other chemical media, notably acids. As previously mentioned the choice of metal oxide also

impacts the tendency to stain and stick to titanium plates which is rather critical for heat exchanger gaskets. Whilst lead oxide is an excellent choice of metal oxide for the end use functionality of plate heat exchanger gaskets it does promote titanium staining. Due to its toxicity and persistence it is not permitted to use this chemical ingredient in many countries around the world including large parts of Europe and USA.

The next section of this paper gives some details of a very extensive study of titanium staining / corrosion and how to avoid it either by polymer selection, using alternative compounding practices or a combination of both.

Titanium Corrosion – Measuring and Prevention via Compounding

Degree of titanium staining has been evaluated by lightly compressing small squares of post cured sheet between titanium sheets, procured via a plate heat exchanger manufacturer, and heat aging them for one week at 200°C. This is considered to be the maximum temperature that gaskets are likely to be subjected to in practice at this time. The results of such a test on two Viton® GBL-900 based compounds in Table 12 are illustrated by the pictures in Figure 7.

Table 12 also indicates the compression set and water swell values achieved using these recipes and it is clear from these data and those in Table 11 that lead oxide is by far the best choice for Viton® GBL-900.

<i>Compound # VT -</i>	<i>10224</i>	<i>10223</i>
<i>Metal Oxide</i>	<i>None</i>	<i>PbO</i>
Viton® GBL-900	100	100
70% PbO Masterbatch		3
Octadecylamine	0.5	0.5
Viton® Process Aid #2	0.5	0.5
MT Carbon Black	30	30
45% Organic Peroxide*	3	3
Triallylisocyanurate	3	3
<i>Hot Water Aged - 168 hrs @ 100 °C</i>		
Volume Swell, %	7.1	0.8
<i>Compression Set 70 hrs @ 200 °C</i>		
Compression Set, % (large buttons)	45.0	33.0

Table 12. Compound Recipes for Initial Titanium Staining Evaluation

*(45% active 2,5-dimethyl 2,5-bis [t-butyl peroxy] hexane on inert filler)

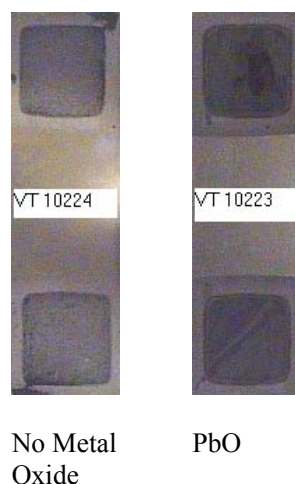


Figure 7. Titanium Staining Result (Viton® GBL-900 with and without lead oxide)

For each compound two small squares of the same post cured sheet were clamped between titanium sheets to provide a duplicate test. The degree of staining shown in Figure 7 is rather high in both cases but distinctly more severe in the case of the lead oxide stabilized compound. A further indication is the force required to pull the test squares from the titanium sheet which was greater in the case of the lead oxide containing compound. Note that compound code VT-10224 contains no metal oxide and compound VT-10223 uses 3 phr of a 70% active lead oxide master batch, typical of the level that might be used in industry. This result is ambiguous in the sense that we cannot determine whether the staining is due to the polymer or compounding ingredients but it is clear that staining is aggravated by the presence of lead oxide. This presents something of a dilemma since we have already shown that lead oxide is necessary to give the low water swell and low compression set required for heat exchanger gaskets when using Viton® GBL-900.

It has been discovered that titanium staining from Viton® GBL-900 based compounds can be improved significantly, in fact eliminated, by including other ingredients in the compound either with or without the presence of lead oxide. The nature of the ingredients that work effectively is such that they are efficient acid acceptors. Examples of chemicals that may be used in this way are hydrophobic silicas and hydrotalcite. The results of staining tests made with lead oxide / hydrotalcite combinations are given below in Figure 8. The compound recipes are given in Table 13.

Compound # VT -	10224	10223	9807	9808	9809	9810
Metal Oxide / Staining Inhibitor	None	PbO	PbO / Silica	Silica	PbO / Hydrotalcite	Hydrotalcite
Viton® GBL-900	100	100	100	100	100	100
70% PbO Masterbatch		3	3		3	
Silica*			3	3		
Hydrotalcite					3	3
Octadecylamine	0.5	0.5	0.5	0.5	0.5	0.5
Viton Process Aid #2	0.5	0.5	0.5	0.5	0.5	0.5
MT Carbon Black	30	30	30	30	30	30
45% Organic Peroxide**	3	3	3	3	3	3
Triallylisocyanurate	3	3	3	3	3	3

Table 13. Evaluation of Titanium Staining Inhibitor Systems - Compound Recipes

*Hydrophobic silica

** (45% active 2,5-dimethyl 2,5-bis [t-butyl peroxy] hexane on inert filler)

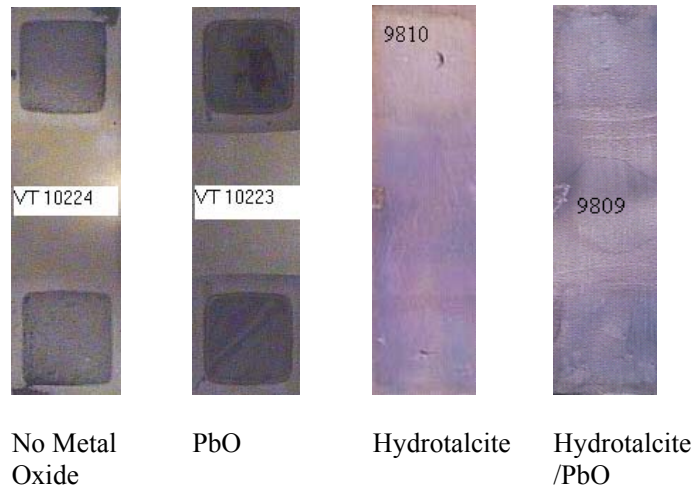


Figure 8. Titanium Staining Result (Viton® GBL-900 with PbO and Hydrotalcite combinations)

The pictures clearly show the elimination of staining when using hydrotalcite in the recipe either with or without the presence of lead oxide. Equal success in terms of eliminating staining can be achieved using hydrophobic silica but there are some potential problems that must be considered.

The data in Tables 13 through 16 show how the other properties of Viton® GBL-900 based compounds are impacted by the use of hydrophobic silica and hydrotalcite as titanium staining inhibitors

<i>Compound # VT -</i>	<i>10224</i>	<i>10223</i>	<i>9807</i>	<i>9808</i>	<i>9809</i>	<i>9810</i>
<i>Metal Oxide / Staining Inhibitor</i>	<i>None</i>	<i>PbO</i>	<i>PbO / Silica</i>	<i>Silica</i>	<i>PbO / Hydrotalcite</i>	<i>Hydrotalcite</i>
Press Cure @ 165°C – Post Cure 16 hrs @ 230°C						
Tensile Strength, MPa	19.9	20.6	22.7	19.4	21.2	23
Elongation @ Break, %	258	201	198	237	185	203
100% Modulus, MPa	5.1	6.8	8	5.6	9	8.6
Hardness, A, pts	74.1	75.1	76.7	76.3	76.3	77.3
Compression Set, % – Large Buttons (336 hrs @ 175°C)	45.0	33.0	33.2	38.6	29.2	31.6

Table 14. Evaluation of Various Staining Inhibitor Systems - Physical Properties and Compression Set Measured @ 23°C

The results in Table 14 indicate that hydrotalcite functions efficiently as an acid acceptor during the curing and post curing phase since the physical properties and compression set resistance are somewhat better than those obtained using lead oxide. Hydrophobic silica

gives higher compression set and shorter elongation at break when used as an alternative to a conventional acid acceptor in this way.

Compound # VT -	10224	10223	9807	9808	9809	9810
Metal Oxide / Staining Inhibitor	<i>None</i>	<i>PbO</i>	<i>PbO / Silica</i>	<i>Silica</i>	<i>PbO / Hydrotalcite</i>	<i>Hydrotalcite</i>
Comments			Fissures	Fissures		
Heat Aged 70 hrs @ 250°C – Property Changes						
% Change, TS	-44.7	-45.6	-41.4	-39.7	-10.8	-40.4
% Change, EB	10.1	-25.4	-20.2	8.4	4.9	21.2
% Change, M-100	-43.1	-14.7	-13.8	-37.5	-8.9	-48.8
pts Change, Shore A	-1.8	-1.2	-0.4	-3.2	-0.8	-3.4

Table 15. Evaluation of Various Staining Inhibitor Systems - Physical Property Retention Measured @ 23°C – Heat Aged 70 hrs @ 250°C

These tests revealed that compounds containing hydrophobic silica had a tendency to fissure during heat aging. The heat aged test pieces from compounds containing either lead oxide alone, hydrotalcite alone or a combination of the two were still perfectly flexible after heat aging. The compound containing a combination of lead oxide and hydrotalcite appears to give outstanding retention of tensile strength. Hydrotalcite gives good heat resistance even when used alone, with retention of tensile strength and elongation at break similar to the lead oxide stabilized compound.

Compound # VT -	10224	10223	9807	9808	9809	9810
Metal Oxide / Staining Inhibitor	<i>None</i>	<i>PbO</i>	<i>PbO / Silica</i>	<i>Silica</i>	<i>PbO / Hydrotalcite</i>	<i>Hydrotalcite</i>
Aged 336 hrs @ 100°C in de-ionized water						
Volume Swell, %	7.1	0.8	0.6	6.7	3.7	6.3

Table 16. Evaluation of Various Staining Inhibitor Systems - Volume Swell Measured @ 23°C - Aged 336 hrs @ 100°C

The water swell results obtained using either hydrophobic silica or hydrotalcite are rather high for these Viton® GBL-900 based compounds, although it is encouraging that the values are in fact lower than those obtained with no metal oxide. Based on additional work not reported here it is estimated that the levels of 3 phr used for both hydrophobic silica and hydrotalcite are excessive and that levels as low as 1 phr would be sufficient to eliminate staining. The water swell of 3.7% obtained with a combination of lead oxide and hydrotalcite is probably acceptable for a gasket application.

Given the advantages in properties and hot water resistance already cited for VTX-8650 vs. Viton® GBL-900, one would expect that compounds based on this new polymer containing hydrotalcite, with or without lead oxide, would give excellent results. VTX-8650 based compounds tested using the limited polymer available at the time of writing of this document confirm its excellent performance as indicated by the data in Tables 17 through 20.

Compound # VT -	10223	9809	10225	10228
Metal Oxide / Staining Inhibitor	PbO	PbO / Hydrotalcite	PbO	PbO / Hydrotalcite
Base Polymer	GBL-900	GBL-900	VTX-8650	VTX-8650
VTX-8650			100	100
Viton® GBL-900	100	100		
70% PbO Masterbatch	3	3	3	3
Hydrotalcite		3		3
Octadecylamine	0.5	0.5	0.5	0.5
Viton® Process Aid #2	0.5	0.5	0.5	0.5
MT Carbon Black	30	30	30	30
45% Organic Peroxide*	3	3	3	3
Triallylisocyanurate	3	3	3	3

Table 17. Evaluation of VTX-8650 vs. Viton® GBL-900 with Hydrotalcite - Compound Recipes

*(45% active 2,5-dimethyl 2,5-bis [t-butyl peroxy] hexane on inert filler)

Compound # VT -	10223	9809	10225	10228
Metal Oxide / Staining Inhibitor	PbO	PbO / Hydrotalcite	PbO	PbO / Hydrotalcite
Base Polymer	GBL-900	GBL-900	VTX-8650	VTX-8650
Tensile Strength, MPa	20.6	21.2	21.1	22.9
Elongation @ Break, %	201	185	306	291
100% Modulus, MPa	6.8	9	4.9	5.8
Hardness, A, pts	75.1	76.3	75.5	74.9
Compression Set, % – Large Buttons (336 hrs @ 175°C)	33.0	29.2	34.0	26.0

Table 18. Physical Properties Measured @ 23°C (Press Cure @ 165°C, Post Cure 16hrs @ 230°C)

The data in Table 18 show that VTX-8650 gives much improved elongation at break vs Viton® GBL-900 and generally improved tensile strength. The VTX-8650 based compound containing a combination of lead oxide and hydrotalcite shows an exceptional balance of physical properties and low compression set.

Compound # VT -	10223	9809	10225	10228
Metal Oxide / Staining Inhibitor	PbO	PbO / Hydrotalcite	PbO	PbO / Hydrotalcite
Base Polymer	GBL-900	GBL-900	VTX-8650	VTX-8650
Heat Aged 70 hrs @ 250°C – Property Changes				
% Change, TS	-45.6	-10.8	-49.3	-44.5
% Change, EB	-25.4	4.9	3.6	5.8
% Change, M-100	-14.7	-8.9	-34.7	-34.5
pts Change, Shore A	-1.2	-0.8	-1.2	0.8

Table 19. Physical Property Retention Measured @ 23°C – Heat Aged 70 hrs @ 250°C

The heat aging data in Table 19 show that VTX-8650 gives similar retention of tensile strength to GBL-900 in these recipes. The exception is the GBL-900 based compound that contains a combination of lead oxide and hydrotalcite.

<i>Compound # VT -</i>	<i>10223</i>	<i>9809</i>	<i>10225</i>	<i>10228</i>
<i>Metal Oxide / Staining Inhibitor</i>	<i>PbO</i>	<i>PbO / Hydrotalcite</i>	<i>PbO</i>	<i>PbO / Hydrotalcite</i>
<i>Base Polymer</i>	<i>GBL-900</i>	<i>GBL-900</i>	<i>VTX-8650</i>	<i>VTX-8650</i>
Aged 336 hrs @ 100°C in de-ionized water				
Volume Swell, %	0.8	3.7	0.8	1.8

Table 20. Volume Swell Measured @ 23°C - Aged 336 hrs @ 100°C

The water swell results show that lead oxide stabilized compounds of VTX-8650 and Viton® GBL-900 have very similar performance but that the addition of hydrotalcite has a much smaller negative impact with the new polymer. As previously mentioned the true level of hydrotalcite required to eliminate staining is probably 1 phr or lower and at such low levels one would expect low water swell when using VTX-8650. Since hydrotalcite also appears to give physical properties, compression set resistance and heat resistance equivalent to lead oxide one would expect a good all round performance with this kind of recipe.

The titanium staining test results for these compounds are given in Figure 9.

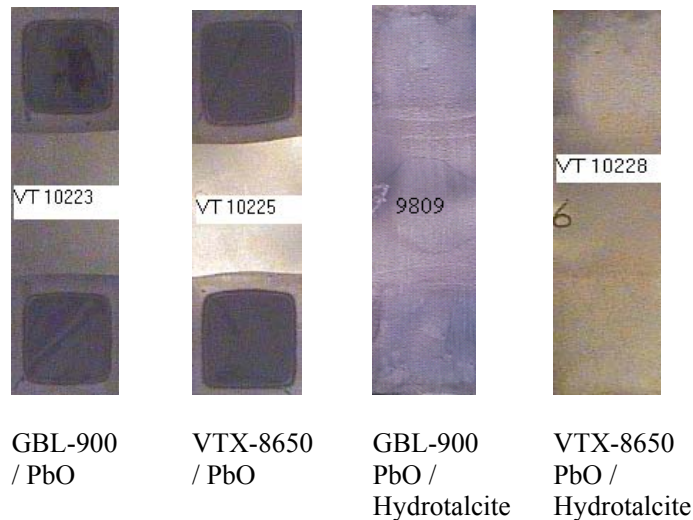


Figure 9. Titanium Staining Result - Evaluation of VTX-8650 vs. Viton® GBL-900 with PbO and Hydrotalcite

There is little difference between the titanium corrosion tendency of VTX-8650 compared to GBL-900 when formulated with lead oxide, although the staining appears to be more localized with VTX-8650. The influence of hydrotalcite at 3 phr in combination with lead oxide is to completely eliminate any sticking or corrosion regardless of the base polymer. In previous tests hydrotalcite has been evaluated in GBL-900 alone and has been shown to

completely eliminate corrosion. It seems reasonable to assume that the same would be true for hydrotalcite containing compounds based on VTX-8650.

Summary and Conclusions

In the early part of this document VTX-8600 and VTX-8650 were introduced as improved alternatives to the other fluoroelastomers for heat exchanger gasket applications. These new grades are based on DuPont Dow's new Advanced Polymer Architecture polymerization technology. Data was presented to illustrate the advantages of the new polymers in terms of mould flow, curing and de-moulding performance. These improvements may permit gasket moulders to more economically manufacture high quality gaskets having excellent end use properties.

Data was also presented to show the generally improved physical properties, compression set resistance and stress relaxation characteristics imparted by the Advanced Polymer Architecture technology.

It was further shown how the heat resistance and the resistance to hot water and acidic media of these new products has been improved to make them more suitable for arduous applications such as plate heat exchanger gaskets. The hot water swell resistance of the new polymers is probably sufficient to allow them to be compounded without the use of lead oxide while retaining functionality in service.

Finally, the essence of a detailed study into ways to reduce the tendency to stain and ultimately corrode titanium heat exchanger plates has been presented. Hydrotalcite provides excellent physical properties and compression set resistance when used either in addition to or without lead oxide. From the data generated it would be expected that corrosion / staining resistant compounds based on Viton® GBL-900 could be formulated using a combination of lead oxide (at 3 phr) and hydrotalcite (at 1 phr or less). This should also give excellent compression set resistance and heat resistance combined with low water swell.

Given the superior nature VTX-8650 vs. Viton® GBL-900 and VTX-8600 vs. Viton® GF, the results of this study suggest that corrosion / staining resistant compounds based on the new polymers may be formulated to have low water swell and good heat and compression set resistance using hydrotalcite as the acid acceptor. This means that lead oxide could probably be eliminated from PHEG recipes based on VTX-8600 and VTX-8650. The new polymers will also certainly bring important advantages in processability and hence the economy of the moulding process.

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