SRT-MTS-935149

ITP Materials Compatibility Issues

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Westinghouse Savannah River Company
EQUIPMENT & MATERIALS TECHNOLOGY
Materials Consultation

Subject Describers
SRT-MTS-935149
IN-TANK PRECIPITATION
BENZENE
GASKETS
RADIATION EFFECTS
SERVICE LIFE
Retention: 5 years

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ITP MATERIALS COMPATIBILITY ISSUES (U)

SUMMARY

Based on review of published chemical resistance and test results, the Materials Consultation Group of E&MT recommends that line gaskets within the ITP process be made of EPDM-bonded Kevlar® (DuPont aramid) fiber, Klinger C-7400 or equivalent. Under the conditions tested, Klinger C-7400 exhibited chemical resistance superior to that of NBR/Kevlar and SBR/Kevlar compounds. Existing Teflon PTFE components such as valve seats, packing, etc. for outside-cell operations are acceptable for a minimum 15-year service life based on radiation exposure calculations provided by ITP engineering and published radiation resistance information. In general, EPDM O-rings and gaskets are acceptable for other applications such as pumps, valves, rotameters, etc. In applications where the concentration of TBP may exceed 1000 ppm, such as injection points, Kalrez® (DuPont), Aflas® (3M), or equivalent compounds are recommended. Viton® compounds are not compatible with high-temperature caustic or TBP-containing solutions. Details on chemical resistance test procedures, results, and radiation resistance are provided.

BACKGROUND

E&MT/Materials Consultation was requested to evaluate the effects of benzene and TBP (Tri-Butyl Phosphate) on the existing gasket materials within the ITP (In-Tank-Precipitation) process. Based on information provided to E&MT/MCG, the SBR-bonded Kevlar gaskets found in service are in non-compliance with the governing P-code (P-112) for the system. P-112 specifies the use of SBR/compressed white asbestos gaskets or NBR-bonded Kevlar® (aramid) as an alternative. The existing gaskets were apparently discovered to be in non-conformance during a shelf-life audit/investigation by QA personnel. A Non-Conformance Report (NCR) was issued and dispositioned to allow the use of the existing gaskets for short-term test purposes (90-day duration).

In addition to not meeting P-code requirements, new chemical additions to the ITP chemistry have made further review of gasket material compatibility necessary. Benzene, generated from the NaTPB (sodium tetraphenylborate) decomposition reaction is to be filtered through stripper columns. In order to control surface reactivity and foaming behavior, TBP is to be added to the process. TBP is a highly effective defoaming agent, but is also highly aggressive towards many polymeric materials. Although the TBP levels necessary to control the foaming behavior are assumed to be low (≈100 ppm), relative effects upon many materials are unknown. Therefore, the compatibility of line gaskets, O-rings, valve seats, etc. required additional review.

Based on information provided by ITP, normal operation will consisted of controlled exposure to benzene and TBP concentrations of 300 and 100 ppm, respectively, in an approximate 5M NaOH solution at temperatures as high as 50° C. Other compounds present in the filtrate solution were much lower in concentration and were not tested. In addition, levels as high as 1000 ppm benzene or TBP may be reached. It is assumed that the TBP will be maintained at a constant concentration to control foaming behavior.

METHODOLOGY

Materials Reviewed

The following materials were reviewed for TBP and benzene compatibility. Materials such as Teflon (PTFE) and flexible graphite (Grafoil®) were not tested due to known excellent chemical resistance.

SBR-bonded Kevlar -	Styrene-Butadiene-Rubber (SBR) has poor resistance to benzene even at moderate concentrations; TBP threshold levels are unknown.
NBR-bonded Kevlar -	Nitrile-Butadiene-Rubber (NBR) has better resistance to benzene than SBR but is known to have poor resistance to moderate concentrations of TBP; threshold levels unknown. Fiber-filled NBR compounds exist, but with higher NBR content.
EPDM-bonded Kevlar -	Ethylene-Propylene Diene Monomer (EPDM) has moderate resistance to benzene and TBP; severe swelling in pure benzene does occur. Mixed results obtained in the past with TBP; threshold levels unknown.
Kevlar-filled Aflas® -	Aflas (3M tetrafluoroethylene-propylene copolymer (TFE/P)) has excellent resistance to caustic solutions and TBP; resistance to benzene is limited.
Kalrez® -	Kalrez (DuPont perfluoroelastomer) has excellent resistance to benzene, TBP, and caustic solutions. Kalrez is relatively expensive and limited in availability.
Viton® A -	All Viton fluoroelastomers have moderate resistance to benzene and caustic solutions, but resistance to TBP is poor even at relatively low levels.
Nordel®	DuPont's EPDM sheet material (unreinforced); Stores stock for general purpose.

Test Program

Because threshold levels of TBP and/or benzene effects upon many polymeric materials are not known, several solutions were mixed in varying concentrations to fully encompass expected operating conditions. Previous work (Reference 1) has indicated that TBP levels as low as 25 ppm can cause significant attack upon some materials. Using a base solution of 5M NaOH, levels of TBP and toluene were varied as shown in Attachment 1. Specific materials tested are listed in Attachment 2. Toluene was used instead of benzene due to carcinogenic exposure concerns, but is considered to affect elastomers to the same degree. In addition, pure TBP and toluene compounds were also included to cover the "worst case" scenario at possible injection points. A solution of 5M NaOH only was also included to distinguish the effects of TBP and toluene from those of NaOH.

Samples of each of the materials were photographed and measured for weight, thickness, and hardness prior to immersion in the various solutions for a 30-day period. Samples were sandwiched between stainless steel washers and immersed to simulate actual service and to eliminate contact between materials. All solution containers were immersed in a water bath and held at approximately 50° C. All TBP-containing solutions were changed out every 7 days to account for the breakdown of TBP into mono- and di-butyl phosphate compounds. Samples were removed after 30 days and allowed to dry for 1 hour prior to measurement of property changes. A Crane mechanical seal was also completely immersed in solution #2 (100 ppm TBP, 300 ppm toluene) for a 30-day period in order to determine the effects of swelling or degradation upon mechanical seal operation. A photograph of this seal prior to immersion is shown in Attachment 3.

RESULTS

Attachment 4 contains a summary of 30-day test results, detailing the change in properties for each material and its respective solution. Changes in weight and thickness are given as percentages of original values, while hardness changes are indicated by actual points lost or gained. Hardness measurements were taken per ASTM D2240-86; +/- 5 points is within tolerance for a given Durometer scale due to its low sensitivity. Therefore, a 5 point change in hardness is not considered significant. Along the same lines, a 10-15% increase in thickness due to swelling is considered acceptable for most static applications. Where tight tolerances are expected, such as mechanical seals, design parameters must be reviewed more closely.

DISCUSSION

Chemical Resistance

Upon review of the test results, a number of observations and conclusions can be drawn. In test solutions 1 and 2 (low TBP), Viton® A exhibits significant swelling and degradation. Klinger C-4401 (NBR/Kevlar) and C-7400 (EPDM/Kevlar) both exhibit only nominal swelling and changes in hardness. C-6401 (SBR/Kevlar) exhibits greater swelling and softening than desired even for these low concentrations of TBP and toluene. As the TBP concentration is increased to 1000 ppm (solution #3), C-6401 (SBR) and Viton® A exhibit severe swelling. The high weight loss of Nordel® in solution #3 is attributed to mechanical damage during sample removal and not direct chemical attack.

As the ratio of toluene to TBP is increased (solutions 4&5), the effects of TBP are negligible. Only nominal changes in weight, thickness, and hardness were observed. As the TBP and toluene levels are balanced in solution 6, higher decreases in thickness are observed. These are attributed to sample retrieval techniques and not actual material loss during immersion, because other property changes are negligible. Solution 7 (5M NaOH) was used as a baseline in an attempt to distinguish TBP and toluene effects from those of NaOH alone. As shown in Attachment 4, p.2, Viton A exhibits a significant decrease in thickness after exposure to NaOH alone. As compared to much lower values for TBP- and toluene-containing solutions, this indicates that the known aggressiveness of NaOH toward Viton A may be inhibited by TBP and/or toluene. C-6401 (SBR) does not exhibit significant swelling in NaOH alone, but is highly sensitive to even low concentrations of TBP and toluene. The high weight increase for Nordel in solution 7 is attributed to improper weighing of the sample; i.e. excessive solution was also included.

In pure TBP (solution 8), C-6401 (SBR) and Viton A compounds are severely swollen and split, resulting in indeterminate weight loss and thickness changes. C-4401 and C-7400 exhibit moderate resistance, with C-7400 showing lower changes in hardness. Surprisingly, Nordel (unreinforced EPDM) showed only slight changes in thickness and weight loss, but with drastic reduction in hardness. Kalrez 1050 exhibited no significant weight change. In pure toluene (solution 9), Mosites 2917 (Aflas) exhibited the greatest weight gain and hardness change along with moderate swelling. C-6401 (SBR) and Viton A showed the highest swelling, 42% and 30%, respectively. C-4401 and C-7400 exhibited only nominal changes, while Kalrez 1050 was practically unaffected.

Teflon vs Radiation

The estimation of service life of polymeric materials in radiation is a complex matter. When reviewing the literature, damage threshold values are inconsistently used. These values are defined as the radiation level at which measurable changes in select physical properties occur. However, these values do not always specify a %change in the property nor do they indicate performance in a given application. Another commonly used value is the 25% damage threshold which defines the level at which 25% loss in a specific property is observed, usually tensile strength or elongation. Some properties are much more sensitive to radiation effects than others and the individual application must be considered. While damage levels are useful for service life estimates, they should not be used to fully evaluate actual performance. A material that loses 25% tensile strength, for example, may still function in its intended application. A good example is that of jumper gasket candidates recently evaluated (Reference 2). Elastomeric compounds with known thresholds in the range of 10^6-10^7 rads still sealed for multiple cycles after 10^8 rads exposure, although significant changes in hardness and flexibility were observed.

Based on the radiation level calculations provided by ITP Engineering (Reference 3), a minimum service life of 15 years is estimated for Teflon PTFE components. This estimate is primarily based on using 5×10^4 rads as the "cutoff" point for measurable radiation damage. This value should not be interpreted as the point at which the material will fail or no longer function adequately. It is simply the point at which significant measurable changes in physical properties are observed. Threshold values between $1\text{-}7 \times 10^4$ rads are found in the literature, depending upon the specific property measured. The 5×10^4 value was chosen based on the nature of most Teflon components where can tolerate some loss in tensile strength. It also accounts for expected downtime and absorption differences between Teflon PTFE and water used in the calculations.

Teflon PTFE components currently installed within the ITP system are judged to be suitable based on the radiation levels expected. If these values are shown to be in error, or too conservative, future components should be evaluated on a case-by-case basis. Alternative materials such as Tefzel® (ETFE, DuPont), PEEK (polyetheretherketone), Ryton® (PPS, Phillips 66), and graphite could be used to replace Teflon PTFE components in high radiation fields, depending upon chemical resistance properties required.

ASSUMPTIONS

During this evaluation, several assumptions were made. First: accumulation of specific chemical compounds was not addressed. A 30-day immersion period was chosen, however, in order to evaluate immediate vs longer-term effects and to quantify changes in physical properties. Second: synergistic effects due to chemical mixtures are impossible to predict without actual testing. Various combinations of TBP and toluene were used in order to account for some effects, but effects from all other compounds in the process solution were not evaluated. Third: radiation dose calculations made by ITP take into account the effects of geometry, volume, and expected operation schedules. These calculations are considered to be relatively accurate considering the difficult nature of predicting actual in-service conditions. The 5×10^4 threshold level used as the "cutoff" point for the service life of Teflon PTFE is conservatively based on "in-air " applications, and radiation resistance in vacuum or liquid has been shown to be higher.

RECOMMENDATIONS

- EPDM-bonded aramid (Kevlar) fiber gasket material (gasket code G-83) is recommended for the line gasket applications within the ITP process. Klinger C-7400 or equivalent is recommended. Filled PTFE gaskets (G-49A & B) may also be used, especially near high concentrations of TBP (injection points, ex.).

- O-rings and seals in process components can be made of Nordel® (EPDM), Aflas®, Kalrez® or equivalent compounds. Viton® is not recommended for long-term service due to poor TBP resistance.

- In-cell, remotely-operated applications such as jumpers should use either Mosites 2917, Klinger C-7400, or their respective equivalents. Multiple use is not considered a high priority, as in canyon operations. Specific chemical resistance should be reviewed.

- Teflon (PTFE) components already installed are judged to be suitable for a minimum of 15 years service, based on radiation exposure calculations provided by ITP. Alternative materials should be considered for applications where higher radiation levels are expected. Specific applications should be reviewed on a case-by-case basis.

- Radiation monitoring equipment should be installed at select locations in order to provide accurate in-service data for process components and/or personnel. This information would be useful in the event of process upsets, unusual occurrences, or component failures.

REFERENCES

1) EED880549, Area Metallurgical Report, Equipment Engineering Department, June 10, 1988, C. F. Jenkins.

2) WSRC-TR-93-382, Rev.0, "Asbestos Gasket Replacement Program, Phase II (U)", July 31, 1993. E. Skidmore, P.N. Bhatt.

3) WER-ITP-93-1016, "Calculated Total Exposure on Gaskets at ITP", E. K. Hansen, June 22, 1993.

4) "Radiation Resistance of Teflon® Resins", The Journal of Teflon®, Jan-Feb., 1969.

5) ASTM D2240-86, " Standard Test Method for Rubber Property - Durometer Hardness".

6) ASTM F146-89, "Standard Test Method for Fluid Resistance of Gaskets".

7) "Radiation Effects on Organic Materials in Nuclear Plants", EPRI NP-2129, Project 1707-3, November 1981.

8) The Radiation Chemistry of Macromolecules, Volume II, Malcolm Dole, 1973, Academic Press.

Peer Review: C F Jenkins

Attachment 1

List of Materials Tested

Material	Manufacturer	Description
C-4401	Klinger	SBR-bonded non-asbestos
C-6401	Klinger	NBR-bonded non-asbestos
C-7400	Klinger	EPDM-bonded non-asbestos
Black Gold 978-C	JM Clipper	Kevlar fiber-filled NBR
Mosites 2917	Mosites Rubber	Kevlar fiber-filled Aflas® (TFE/P)
Viton® A	Dupont (resin)	unreinforced fluoroelastomer (hexafluoropropylene copolymer)
Kalrez® 1018/1050	DuPont (resin)	unreinforced perfluoroelastomer
Craneplast®	John Crane	EPDM O-ring for Crane mechanical seals

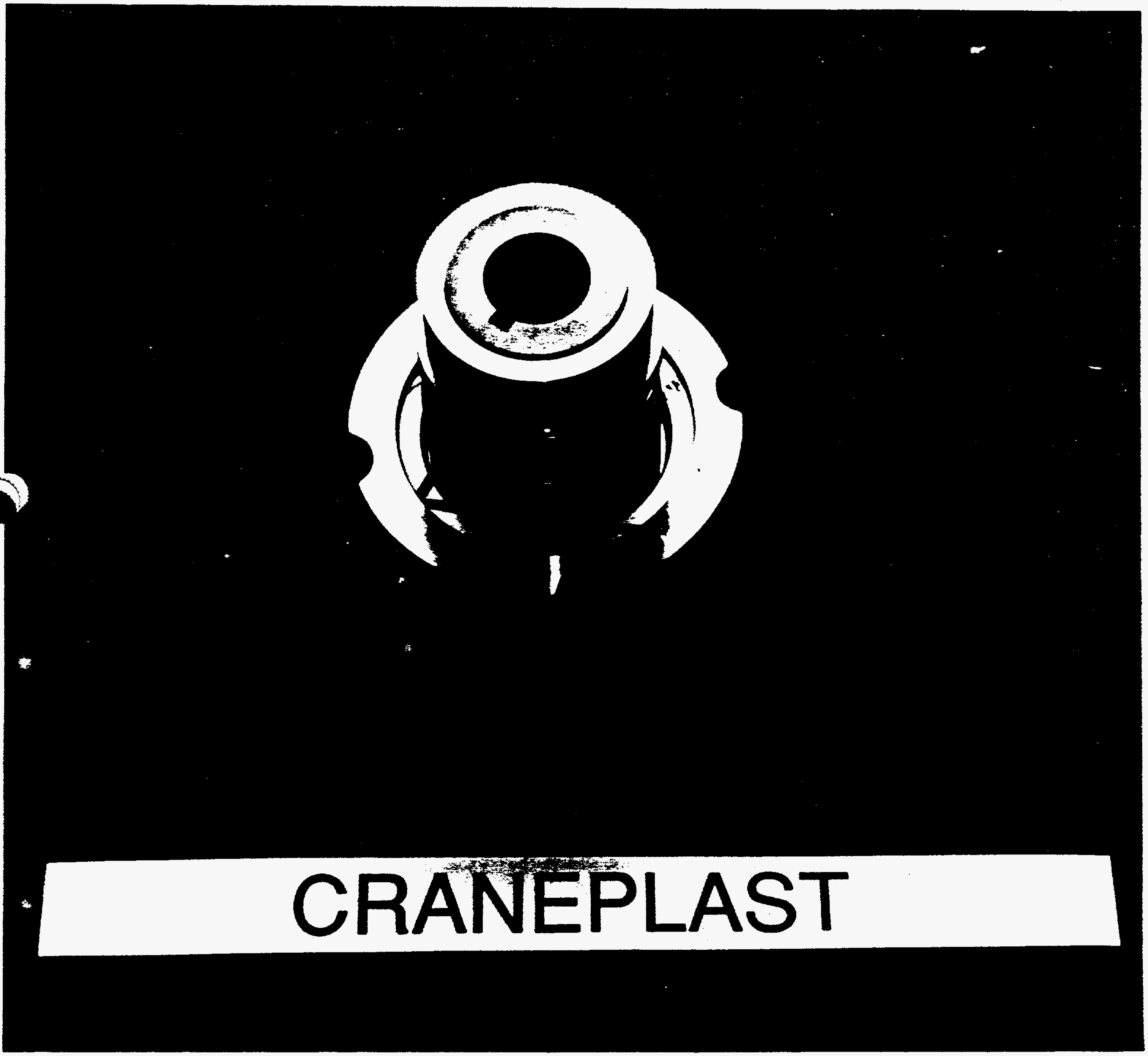
Attachment 2

Test Solution Compositions

Solution #	Base	Tri-butyl phosphate (TBP)	Toluene
1	5M NaOH	10 ppm	300 ppm
2	5M NaOH	100 ppm	300 ppm
3	5M NaOH	1000 ppm	300 ppm
4	5M NaOH	10 ppm	1000 ppm
5	5M NaOH	100 ppm	1000 ppm
6	5M NaOH	1000 ppm	1000 ppm
7	5M NaOH only		
8	-------------	TBP only	----------
9	-------------	------------	Toluene only

Attachment 3

Photograph of mechanical seal prior to immersion (O-ring Internal)



Attachment 4 - Summary of Chemical Resistance Test Results (p.1)

Solution #	Wi	Wf	%ΔW	Ti	Tf	%ΔT	Hi	Hf	ΔH
	(before)	(after)		(before)	(after)		(before)	(after)	
#1									
C-4401	1.90	2.08	9.63	0.07	0.07	5.97	90	80	-10
C-6401	3.13	3.39	8.55	0.07	0.08	20.90	95	75	-20
C-7400	1.61	1.66	3.10	0.07	0.07	-4.41	90	80	-10
978-C	3.46	3.72	7.59	0.12	0.13	5.83	80	50	-30
Viton A	1.05	1.17	11.10	0.06	0.10	75.00	70	65	-5
2917	3.66	3.68	0.58	0.14	0.14	3.68	80	70	-10
Nordel	0.82	0.83	0.75	0.07	0.08	14.29	70	50	-20
#2									
C-4401	1.91	2.11	10.20	0.07	0.07	8.96	90	80	-10
C-6401	2.83	3.01	6.36	0.07	0.07	2.94	95	60	-35
C-7400	1.53	1.56	2.31	0.07	0.07	-2.90	90	80	-10
978-C	3.39	3.61	6.31	0.12	0.13	5.79	80	75	-5
Viton A	1.00	1.08	8.72	0.06	0.08	41.07	70	65	-5
2917	4.11	4.14	0.76	0.14	0.15	10.29	80	75	-5
Nordel	0.88	0.88	0.77	0.07	0.08	15.71	70	50	-20
#3									
C-4401	1.86	2.01	7.69	0.07	0.07	-1.45	90	95	5
C-6401	3.10	2.04	-34.19	0.07	0.09	34.33	95	85	-10
C-7400	1.60	1.61	0.42	0.07	0.07	1.47	90	85	-5
978-C	3.32	3.70	11.25	0.12	0.13	9.84	80	90	10
Viton A	1.01	1.20	19.23	0.06	0.09	51.79	70	65	-5
2917	4.06	4.00	-1.35	0.14	0.14	4.35	80	80	0
Nordel	0.81	0.71	-11.47	0.07	0.07	5.71	70	60	-10
#4									
C-4401	1.91	2.07	8.65	0.07	0.08	15.38	90	90	0
C-6401	2.92	3.11	6.41	0.07	0.08	14.93	95	85	-10
C-7400	1.61	1.64	1.68	0.07	0.06	-5.88	90	85	-5
978-C	3.40	3.64	7.06	0.12	0.13	10.74	80	90	10
Viton A	1.01	1.09	8.18	0.06	0.06	12.50	70	75	5
2917	3.75	3.85	2.66	0.14	0.16	14.60	80	75	-5
Nordel	0.68	0.69	0.56	0.07	0.08	8.57	70	65	-5

Attachment 4 - Summary of Chemical Resistance Test Results (p.2)

Solution #	Wi	Wf	%ΔW	Ti	Tf	%ΔT	Hi	Hf	ΔH
	(before)	(after)		(before)	(after)		(before)	(after)	
#5									
C-4401	1.89	2.06	9.21	0.07	0.06	-7.25	90	90	0
C-6401	1.90	3.34	76.42	0.07	0.07	4.48	95	80	-15
C-7400	1.60	1.67	4.18	0.07	0.06	-7.25	90	80	-10
978-C	3.43	3.58	4.40	0.12	0.13	4.13	80	70	-10
Viton A	1.07	1.19	11.69	0.06	0.06	1.79	70	75	5
2917	4.15	4.16	0.31	0.14	0.14	5.15	80	70	-10
Nordel	0.90	0.81	-9.74	0.08	0.07	-8.00	70	60	-10
#6									
C-4401	1.88	2.04	8.72	0.07	0.06	-10.14	90	90	0
C-6401	1.75	1.87	6.65	0.07	0.06	-11.94	95	90	-5
C-7400	1.60	1.62	1.48	0.07	0.06	-10.14	90	80	-10
978-C	3.44	3.68	6.96	0.12	0.12	0.00	80	80	0
Viton A	1.08	1.13	4.89	0.06	0.05	-7.14	70	65	-5
2917	4.04	4.17	3.37	0.14	0.15	5.84	80	80	0
Nordel	0.71	0.72	1.05	0.08	0.07	-11.84	70	60	-10
#7									
C-4401	1.89	2.06	9.22	0.06	0.07	6.35	90	90	0
C-6401	1.91	2.06	7.73	0.07	0.07	0.00	95	90	-5
C-7400	1.57	1.65	4.94	0.07	0.06	-11.59	90	80	-10
978-C	3.45	3.68	6.54	0.12	0.12	1.65	80	80	0
Viton A	1.03	1.21	17.60	0.06	0.05	-19.64	70	60	-10
2917	4.11	4.18	1.68	0.14	0.13	-2.19	80	70	-10
Nordel	0.71	0.91	28.29	0.07	0.08	2.70	70	60	-10
#8									
C-4401	1.89	2.30	21.62	0.07	0.09	36.36	90	70	-20
C-6401	1.88	n/a	n/a	0.07	n/a	n/a	95	n/a	n/a
C-7400	1.62	1.80	11.64	0.07	0.08	14.71	90	85	-5
978-C	3.47	4.03	16.08	0.12	0.14	18.03	80	75	-5
Viton A	1.03	2.26	119.41	0.06	n/a	n/a	70	n/a	n/a
2917	3.93	4.15	5.49	0.14	0.15	9.42	80	60	-20
Nordel	0.71	0.70	-0.75	0.08	0.07	-8.00	80	55	-25
Kalrez 1050	0.33	0.34	0.42	0.07	0.07	2.86	80	80	0
#9									
C-4401	1.88	2.02	7.21	0.07	0.07	9.23	90	90	0
C-6401	1.89	2.07	10.00	0.07	0.10	41.79	95	85	-10
C-7400	1.60	1.80	12.37	0.07	0.07	5.88	90	90	0
978-C	3.24	3.52	8.73	0.12	0.13	8.33	80	90	10
Viton A	1.03	1.07	3.98	0.06	0.07	30.36	70	75	5
2917	3.90	4.58	17.36	0.14	0.17	23.53	80	60	-20
Nordel	0.79	0.79	-0.16	0.08	0.11	44.74	70	60	-10
Kalrez 1050	0.20	0.20	0.00	0.07	0.07	0.00	80	80	0