Minimizing Glovebox Glove Breaches, Part III: Deriving Service Lifetimes

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ABSTRACT

At the Los Alamos Plutonium Facility, various isotopes of plutonium along with other actinides are handled in a glove box environment. Weapons-grade plutonium consists mainly in Pu-239. Pu-238 is another isotope used for heat sources. The Pu-238 is more aggressive regarding gloves due to its higher alpha-emitting characteristic (~300 times more active than Pu-239), which modifies the change-out intervals for gloves. Optimization of the change-out intervals for gloves is fundamental since Nuclear Materials Technology (NMT) Division generates approximately 4 m^3/yr of TRU waste from the disposal of glovebox gloves. To reduce the number of glovebox glove failures, the NMT Division proactively investigates processes and procedures that minimize glove failures. Aging studies have been conducted that correlate changes in mechanical (physical) properties with degradation chemistry. This present work derives glovebox glove change intervals based on mechanical data of thermally aged Hypalon®, and Butasol® glove samples. Information from this study represent an important baseline in gauging the acceptable standards for polymeric gloves used in a laboratory glovebox environment and will be used later to account for possible presence of dose-rate or synergistic effects in "combined-environment." In addition, excursions of contaminants into the operator's breathing zone and excess exposure to the radiological sources associated with unplanned breaches in the glovebox are reduced.

INTRODUCTION

Nuclear Materials Technology (NMT) Division programmatic operations involve working with various amounts of plutonium and other highly toxic, alpha-emitting materials. The spread of radiological contamination and excursions of contaminants into the operator's breathing zone is prevented through the use of a variety of gloveboxes. The glovebox gloves are the weakest part of this engineering control. Thus, the minimization of unplanned breaches in the glovebox, e.g., glove failures, is a primary concern in the daily operations. To reduce the number of glovebox glove failures, the NMT Division proactively investigates processes and procedures that reduce glove failures. This is the third paper on this issue [Ref. 1].

At the Los Alamos Plutonium Facility (PF4) glovebox gloves are exposed to elevated temperatures and exceptionally aggressive radiation environments. Weapons-grade plutonium consists mainly in Pu-239. Pu-238 is another isotope used for heat sources. In terms of radiation damage, the Pu-238 is more aggressive regarding gloves due to its higher alpha-emitting characteristic (~300 times more active than Pu-239). A dramatic example of this "combined-environment," radioactive and thermal characteristics, is shown in Fig. 1.

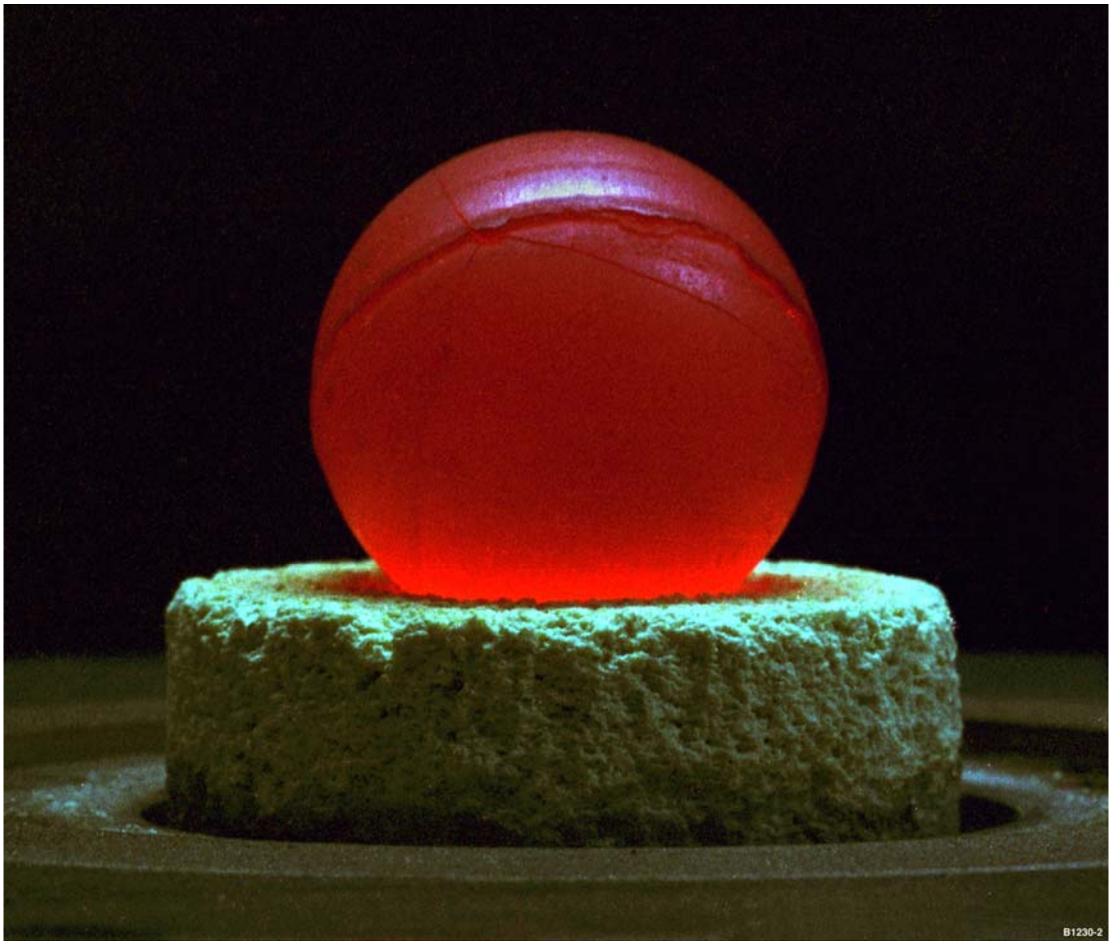

Fig. 1. A golf-ball size amount of Pu-238 metal

Predictive models are needed to estimate glovebox glove service lifetimes, i.e. change-out intervals. Towards this aim aging studies have been conducted that correlate changes in mechanical (physical) properties with degradation chemistry. The focus of this present work derives glovebox glove change intervals based on previously reported and unreported mechanical data of thermally aged Hypalon®, and Butasol® glove samples [Ref. 2]. The paper begins with a review of the properties of the glovebox glove materials and what is expected when these materials are exposed to an elevated temperature, followed by a discussion of the material specification and how change-out intervals are derived, the experimental methodology, results, and summary.

GLOVEBOX GLOVE MATERIALS

The glovebox gloves made from Hypalon® (hereafter referred to as hypalon) are the workhorses of NMT Division programmatic operations due to its superior properties. Around 90 percent of the glovebox gloves in use within PF4 are made of this material. Hypalon material is resistant to interactions with alcohols and strong acids and bases. This material also exhibits excellent ultraviolet light and oxygen stability. The useful temperature range is -50°C to 160°C. The tri-layered hypalon/lead oxide-neoprene/hypalon material exhibits the same chemical resistances and stability, but possesses additional utility in radiolytic environments. Glovebox gloves with a lead-oxide inner liner reduce exposure to workers from beta-particles, x-rays, and weak gamma-rays. Lead-oxide is incorporated into the rubber gloves during fabrication as a dense medium to attenuate radiation and adds a measure of protection for glovebox workers. Lead oxide is the material of choice as the absorption medium because of its high mass absorption coefficient for x-rays, relatively high density, and it's compatibility with rubber in the fabrication process.

Glovebox gloves made of Butasol® (hereafter referred to as butasol) represent the second largest type of glove used in NMT Division gloveboxes. Butasol is essentially butyl rubber. The elastomer is an isoprene – isobutylene copolymer rubber. Butasol is characterized with very good gas permeation, ozone, and heat resistance and has the best barrier to water vapor, gasses, and certain toxic chemicals. It is resistant to animal and vegetable fats, oils, greases, ozone, and strong oxidizing chemicals. Butasol is attacked by petroleum solvents, coal tar solvents, and aromatic hydrocarbons. The useful temperature range is 10°C to 135°C.

Hypalon possesses chemical functionalities such as chloro- and sulfochloro-groups, which are highly susceptible to thermal aging. In degradation studies of chlorosulfonated polyethylene materials thermal aging has resulted in loss of -SO_2Cl groups and dehydrochlorination [Ref. 2]. Both polymers may degrade through main chain breakdown (scissoring), oxidation, and polymer cross-linking. An example of one of these pathways is shown in Fig. 2.

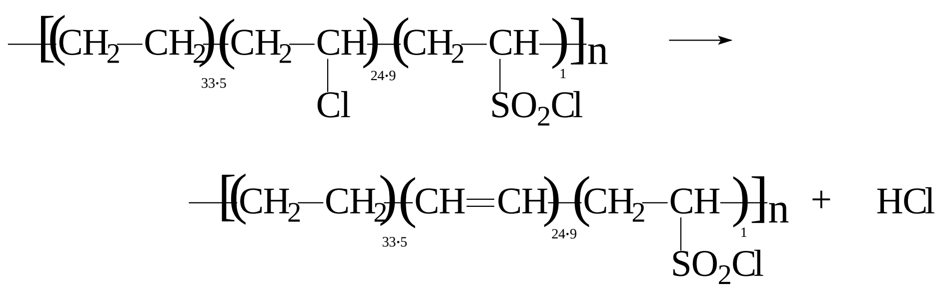

Fig. 2. Example of a dehydrochlorination pathway

When oxidative and scissoring degradation are the predominate effect, lower molecular weight [Ref. 3], decreased mechanical stability [Ref. 4] and often decreased chemical inertness [Ref. 4-7] are observed. The tensile properties (modulus and "ultimate elongation") of materials with degradation pathways should demonstrate a softening of the material with aging time. With oxidative cross-linking, and dehydrohalogenation the opposite effects are expected. Oxidative cross-linking and dehydrohalogenation should show a stiffening of the material with aging time. When enough double bonds are formed from the dehydrohalogenation mechanism, a visual discoloration should be observed. An example of this effect is shown in Fig. 3.

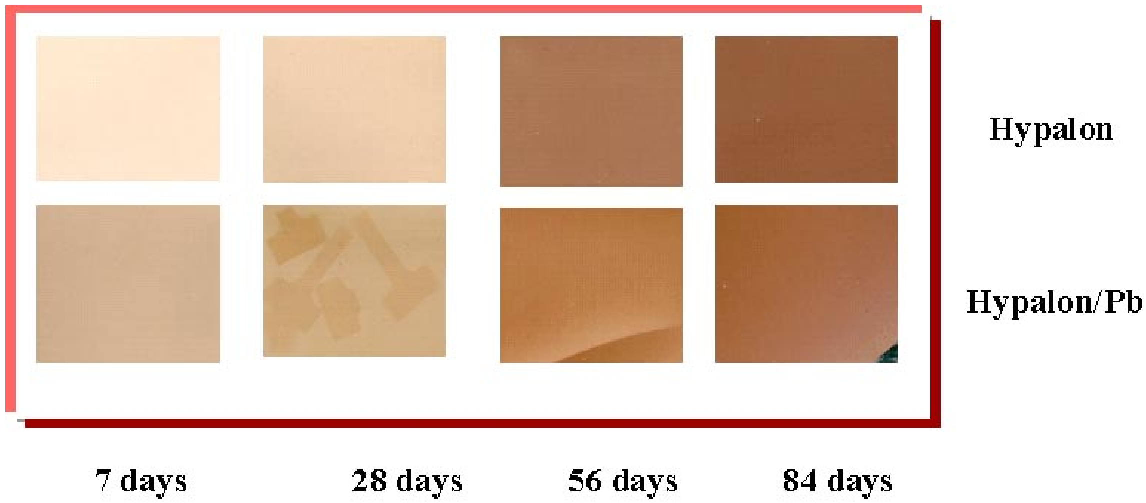

Fig. 3. Color change correlates with Hypalon material heated at 120ºC.

MECHANICAL PROPERTY SPECIFICATIONS

For use in PF4, specifications for the hypalon gloves (HYP), 0.762 mm tri-layered hypalon/lead glovebox gloves (TLH), and 0.762 mm butasol glovebox gloves (BUT) have already been established [Ref. 8]. The relevant mechanical properties are shown on Table I.

Table I. Mechanical Property Specifications

Property	HYP	TLH	BUT
Tensile Strength (Pa)	1.31E+07	8.27E+06	1.24E+07
Ultimate Elongation (%)	500	300	600
Toughness (Pa)	2.07E+07	2.41E+07	

Mechanical property specifications for hypalon apply to both 0.381 and 0.762 mm thickness. Tensile strength is defined as the maximum load applied in breaking a tensile test piece divided by the original cross-sectional area of the test piece (also termed maximum stress and ultimate tensile stress). Ultimate elongation is the elongation at time of rupture (also termed maximum strain). ASTM D412-97 is the applicable standard used [Ref. 9]. The specification for the tensile test and ultimate elongation are the minimum acceptable values. In addition, the ultimate elongation must not vary 20% from the original value. If the tensile strength specification cannot be met, then the toughness specification must be met. The most important material property to consider is the toughness. Toughness is the integral under the engineering stress versus strain curve (those generated during tensile testing), which is the total force required to take the sample from its initial unstressed state to failure. The value for toughness is more important than the value for maximum stress, because maximum stress gives no indication about the energy required to reach that maximum value. No toughness value for butasol has been determined as of yet.

In order to establish service lifetimes for glovebox gloves in a thermal environment, the mechanical properties of glovebox glove materials in controlled convection ovens were studied. Once a sample falls out of specification, the change out interval is set at the previous analyses date. For example, if the sample of hypalon material heated at 100ºC for 21 days shows a tensile strength of 1.24E+07 Pa, this is out of specification. And if the previous sample at 14 days was in specification with a tensile strength of 1.34E+07 Pa, the change out interval is set at 14 days. The experimental details for the hypalon samples have been previously published [Ref. 2]. The experimental settings for butasol samples are presented next.

EXPERIMENTAL

Materials

Planchets (9cm X 9cm) were cut from a pair of butasol glovebox gloves. All gloves were used as received from North Safety Products (Cranston, RI).

Sample Aging

The aging experiments were performed in controlled convection ovens at four temperatures: 60, 80, 100, and 120ºC. Samples were suspended in the oven to allow air to circulate freely around them. The samples were removed from the oven after a period of time between 1 and 127 days for analyses.

Rheological Instrumentation

The tensile properties of the aged samples were determined on an Instron Model 4483, Universal Electromechanical Test frame using the Series IX Materials Testing Software. The testing regime for the glove sample was from ASTM D 412-98a. Samples were strained at a rate of 10 in./min at room temperature with an initial jaw separation of 2.54 cm. A 100 N transducer was used for all measurements. Typically 5 samples were tested and the data were averaged to obtain the results for each aging time. Dimensions of the dog-bone shaped samples were: total length, 3.81 cm; narrow section length, 2.54 cm; width (dog-bone ends) 1.59 cm width (narrow section), 0.48 cm.

RESULTS

A listing of the mechanical data for the hypalon (HYP), hypalon tri-layer (TLH), and butasol (BUT) aged samples is shown in Table II-IV. Tensile strength and ultimate elongation are listed as stress and strain, respectively. Although modulus data is not part of the specification, it is included in the results because the modulus of a material is a measure of the stiffness and is defined as the ratio of stress to strain, or the strength relative to elongation. The modulus reported here is the initial modulus. Fields highlighted in bold fail the minimum acceptable values.

Table II. Tensile Data for Samples of Hypalon

Time (Days)	Tensile Data Modulus (Pa)	Stress (Pa)	Strain	Toughness (Pa)
60ºC				
0	6.62E+06	2150	530%	3.97E+07
1	5.54E+06	1.56E+07	537%	4.08E+07
3	5.82E+06	1.59E+07	527%	4.09E+07
5	6.01E+06	1.60E+07	534%	4.19E+07
7	6.02E+06	1.54E+07	**491%**	3.74E+07
14	4.01E+06	1.55E+07	**498%**	3.84E+07
21	6.23E+06	1.63E+07	**476%**	3.89E+07
28	7.12E+06	1.60E+07	**462%**	3.78E+07
56	6.98E+06	1.57E+07	**424%**	3.51E+07
88	7.21E+06	1.70E+07	**426%**	3.66E+07
98	7.23E+06	1.74E+07	**422%**	3.75E+07
80ºC				
0	6.62E+06	1.48E+07	530%	3.97E+07
1	6.05E+06	1.40E+07	541%	3.95E+07
3	6.25E+06	1.33E+07	**474%**	3.42E+07
5	6.06E+06	1.40E+07	**492%**	3.59E+07
7	6.60E+06	1.43E+07	**470%**	3.56E+07
14	7.03E+06	1.47E+07	**424%**	3.36E+07
21	6.99E+06	1.49E+07	**414%**	3.37E+07
28	6.44E+06	1.43E+07	**386%**	3.04E+07
56	7.06E+06	1.47E+07	**360%**	2.90E+07
100ºC				
0	6.62E+06	1.48E+07	530%	3.97E+07
1	6.13E+06	1.40E+07	513%	3.76E+07
3	6.97E+06	1.40E+07	**461%**	3.50E+07
5	7.58E+06	1.38E+07	**442%**	3.36E+07
7	8.01E+06	1.42E+07	**405%**	3.16E+07
14	8.35E+06	1.42E+07	**394%**	3.06E+07
21	7.64E+06	1.40E+07	**380%**	2.97E+07
28	7.65E+06	1.45E+07	**389%**	3.16E+07
56	8.17E+06	1.53E+07	**378%**	3.28E+07
120ºC				
0	6.62E+06	1.48E+07	530%	3.97E+07
1	5.85E+06	1.57E+07	**483%**	3.87E+07
3	6.25E+06	1.63E+07	**460%**	4.04E+07
5	7.16E+06	1.54E+07	**410%**	3.59E+07
7	7.47E+06	1.55E+07	**373%**	3.32E+07
14	6.58E+06	1.63E+07	**260%**	2.41E+07
21	8.73E+06	1.75E+07	**175%**	**1.54E+07**
28	1.27E+07	1.87E+07	**110%**	**9.25E+06**

Table III. Tensile Data for Samples of Hypalon Tri-layer

Time (Days)	Tensile Data			
	Modulus (Pa)	Stress (Pa)	Strain	Toughness (Pa)
60ºC				
0	7.72E+06	1.24E+07	400%	2.92E+07
1	7.84E+06	1.28E+07	368%	2.80E+07
3	8.35E+06	1.32E+07	370%	2.87E+07
5	8.48E+06	1.30E+07	364%	2.80E+07
7	8.41E+06	1.27E+07	350%	2.69E+07
14	6.98E+06	1.33E+07	363%	2.84E+07
21	7.41E+06	1.32E+07	344%	2.74E+07
28	7.72E+06	1.33E+07	337%	2.73E+07
56	8.53E+06	1.31E+07	**309%**	3.51E+07
88	9.69E+06	1.31E+07	327%	3.66E+07
98	8.40E+06	1.31E+07	**312%**	2.51E+07
80ºC				
0	7.72E+06	1.24E+07	400%	2.92E+07
1	7.58E+06	1.17E+07	343%	2.44E+07
3	8.49E+06	1.20E+07	349%	2.54E+07
5	8.74E+06	1.19E+07	338%	2.45E+07
7	8.59E+06	1.15E+07	321%	**2.28E+07**
14	9.25E+06	1.22E+07	**318%**	**2.40E+07**
21	9.37E+06	1.23E+07	320%	2.45E+07
28	9.54E+06	1.19E+07	**302%**	**2.27E+07**
56	1.03E+07	1.14E+07	**260%**	**1.87E+07**
100ºC				
0	7.72E+06	1.24E+07	400%	2.92E+07
1	7.91E+06	1.16E+07	333%	**2.35E+07**
3	8.49E+06	1.13E+07	**313%**	**2.19E+07**
5	8.82E+06	1.08E+07	**301%**	**2.05E+07**
7	9.57E+06	1.08E+07	**279%**	**1.91E+07**
14	1.12E+07	1.01E+07	**198%**	**1.24E+07**
21	1.12E+07	9.94E+06	**190%**	**1.18E+07**
28	1.29E+07	9.63E+06	**151%**	**9.01E+06**
56	2.12E+07	8.89E+06	**97%**	**5.62E+06**
120ºC				
0	7.72E+06	1.24E+07	400%	2.92E+07
1	9.26E+06	1.11E+07	**245%**	**1.67E+07**
3	2.03E+07	**8.23E+06**	**98%**	**5.23E+06**
5	3.62E+07	**7.76E+06**	**50%**	**2.66E+06**
7	9.76E+07	9.51E+06	**21%**	**1.32E+06**
14	4.37E+07	**4.70E+06**	**6%**	**1.72E+05**
21	4.26E+07	**4.07E+06**	**7%**	**2.07E+05**
28	-	-	-	-

Table IV. Tensile Data for Samples of Butasol

Time (Days)	Tensile Data Modulus (Pa)	Stress (Pa)	Strain	Toughness (Pa)
60ºC				
0	3.74E+06	**1.15E+07**	663%	2.86E+07
1	3.85E+06	1.35E+07	725%	3.58E+07
3	4.27E+06	1.26E+07	701%	3.26E+07
7	3.72E+06	1.33E+07	690%	3.39E+07
14	3.42E+06	1.32E+07	692%	3.40E+07
42	3.79E+06	1.37E+07	687%	3.54E+07
70	3.69E+06	1.36E+07	675%	3.49E+07
99	3.68E+06	1.38E+07	672%	3.56E+07
127	3.48E+06	1.30E+07	633%	3.20E+07
80ºC				
0	3.74E+06	**1.15E+07**	663%	2.86E+07
1	3.61E+06	1.42E+07	729%	3.77E+07
3	3.84E+06	1.27E+07	652%	3.12E+07
7	3.77E+06	1.35E+07	691%	3.52E+07
14	3.67E+06	1.38E+07	672%	3.54E+07
42	3.47E+06	1.32E+07	619%	3.23E+07
70	3.45E+06	1.36E+07	610%	3.29E+07
99	3.11E+06	**1.22E+07**	**585%**	2.85E+07
127	3.45E+06	1.38E+07	624%	3.46E+07
100ºC				
0	3.74E+06	**1.15E+07**	663%	2.86E+07
1	4.05E+06	1.41E+07	658%	3.59E+07
5	3.65E+06	1.19E+07	570%	2.74E+07
7	3.36E+06	1.29E+07	600%	3.06E+07
14	3.39E+06	1.40E+07	617%	3.42E+07
42	3.12E+06	1.29E+07	644%	3.26E+07
70	3.26E+06	1.25E+07	661%	3.30E+07
99	2.79E+06	**1.17E+07**	661%	3.05E+07
127	2.81E+06	**1.23E+07**	656%	3.24E+07
120ºC				
0	3.74E+06	**1.15E+07**	663%	2.86E+07
1	3.85E+06	1.44E+07	631%	3.56E+07
3	4.27E+06	1.42E+07	641%	3.56E+07
7	3.72E+06	1.26E+07	708%	3.47E+07
14	3.42E+06	**1.09E+07**	791%	3.33E+07
21	3.93E+06	**9.54E+06**	**802%**	3.02E+07
42	3.79E+06	**4.90E+06**	**899%**	1.91E+07
70	3.69E+06	**3.18E+06**	**923%**	1.41E+07
99	3.68E+06	**1.85E+06**	**983%**	9.83E+06
127	3.48E+06	**1.23E+06**	766%	5.90E+06

Based on the specification in Table I and the results shown in Tables II-IV, the recommended change-out intervals for hypalon (HYP), hypalon tri-layer (TLH), and butasol (BUT) glovebox gloves from North Safety Products are listed in Table V. Less conservative values for the change-out intervals can be obtained through extrapolate, using Arrhenius plots or similar methods [Ref. 10]. Activation energy values would have to be derived to determine reaction rates for breakdown mechanisms at both ambient and elevated temperatures. Recommended change-out intervals for room temperature applications have been discussed in a previous report [Ref. 1b].

Table V. Recommended Change-out Intervals for North Glovebox Gloves in a Thermal Environment

Temperature	Glove Material		
	HYP	**TLH**	**BUT**
20ºC	3 years	3 years	2 years
60ºC	5 days	28 days	2 years
80ºC	1 day	5 days	2 years
100ºC	1 day	< 1 day	70 days
120ºC	< 1 day	< 1 day	7 days

DISCUSSION

Glovebox gloves materials made from hypalon that were stored at ambient temperature and used as control samples met the acceptance criteria. Glovebox gloves material made from butasol was below specification due to tensile strength, although it was within the uncertainty limits of the testing instrument (±1.0 E+06 Pa). The modulus and strain for the 120ºC samples of the hypalon/lead-neoprene/hypalon tri-layered begin their erosion with no induction period and degrade to brittleness such that no tensile data can be collected after 21 days of thermal aging. In general, all three materials become out of specification because the aging causes the strain to drop below the minimum specification. The tensile properties of the hypalon/lead-neoprene/hypalon tri-layered material degrade more quickly and more extensively compared to the hypalon material, although it is the latter that falls out of specification sooner. Samples of the tri-layer hypalon at 60ºC (56, 98 days) dropped out of specification solely due to the variation in ultimate elongation. Additionally, samples of the tri-layer hypalon at 80ºC (7 days) and 100ºC (1 day) dropped out of specification solely due to the toughness specification. The increase in modulus for the hypalon samples correlate with oxidative cross-linking and dehydrohalogenation show a stiffening of the material with aging time. As previously reported, -C=C- and -C=O formation represent the primary degradation mechanisms that correlate with the changes in tensile properties [Ref. 2]. The decrease in modulus for the butasol samples correlate with main chain breakdown show a softening of the material with aging time.

The information in Table I will be used to modify glovebox glove maintenance procedures. The initial temperature range studied (60 - 120ºC) represent extreme thermo environments. In the future, an aging study should be conducted in the more practical temperature range of 20 - 60ºC. Nevertheless, results from this investigation are applicable to glovebox operations with hot plates, furnaces, and Pu-238. Glovebox gloves that are near hot plates and furnaces should be assessed for heat damage. Pu-238 heat sources can reach temperatures between 85 and 450ºC [Ref. 11]. If the hot surfaces of the heat sources or storage containers are touched, the glovebox gloves should be immediately inspected and replaced if visual discoloration in the area where the hot surfaces touched the glove is noticed. It should be noted that the change-out intervals recommendation derived in this study are formulation-specific; they should not be assumed to apply to other formulation of the same generic material classes, i.e. gloves made from other companies. Formulation differences, particularly with regard to the identity and amount of stabilizing additives, can exert a strong influence on the thermal resistance of a given material.

Optimization of the change-out intervals for gloves is fundamental since NMT Division generates approximately 4 m^3/yr of TRU waste from the disposal of glovebox gloves. More waste is generated when unplanned breaches in the glovebox, e.g., glove failures occur. In addition to waste generation, significant costs are incurred from a contamination incident due to the loss in production, cost of the cleanup, and preparation of incident documentation. Last, excursions of contaminants into the operator’s breathing zone and excess exposure to the radiological sources associated with unplanned breaches in the glovebox are reduced. The next paper in this serial will report on the radiological effects of Pu-238 and Pu-239.

CONCLUSION

Aging studies have been conducted that correlate changes in mechanical (physical) properties with degradation chemistry. We have derived a general methodology for calculating glovebox glove change-out intervals from tensile data. Under various temperatures stress, strain, and toughness were measured. The resulting data is compared to product specifications. Once the tensile data is out of specification, the recommended change-out date is reached. Information from this study represent an important baseline in gauging the acceptable standards for polymeric gloves used in a laboratory glovebox environment and will be used later to account for possible presence of dose-rate or synergistic effects in “combined-environment.”

REFERENCES

1. (a) Cournoyer, M.E.; Andrade, R.M.; Zaelke, R.L.; Maestas, M.M. and Balkey, J.J. (2005) Minimizing Glovebox Glove Failures: Part II, LA-UR 04-6146, *Journal of the American Society of Mechanical Engineers*, Proceeding from WM’05, February 28 – March 3, 2005. (b) Cournoyer, M.E.; Casey, J.W.; Taylor, D.J.; Stimmel, J.J.; Zaelke, R.L.; and Balkey, J.J. “Minimizing Glovebox Glove Failures,” LA-UR 04-1144, *Journal of the American Society of Mechanical Engineers*, Proceeding from WM’04, February 29 – March 4, 2004.
2. Wilson. K.V.; Smith, B.L.; MacDonald, J.M.; Schoonover, J.R.; Castro, J.M.; Smith, M.E.; Cournoyer, M.E.; Marx, R.; Steckle, W.P. (2004) *Polymer Degradation and Stability* 84: 439-449. Unpublished results from Kennard V. Wilson, MST-7, Los Alamos National Laboratory.
3. Lunkwitz, K.; Burger, W.; Geissler, U.; Petr, A.; Jehnichen, D. (1996) *Journal of Applied Polymer Science 60*(11): 2017-2024.
4. Abdou, S.A.; Mohamed, R.I. (2002) *Journal of Physics and Chemistry of Solids 63*(3): 393-398.
5. Lappan, U.; Haussler, L.; Pompe, G.; Lunkwitz, K. (1997) *Journal of Applied Polymer Science* 66(12): 2287-2291.

6. Schierholz, K.; Lappan, U.; Lunkwitz, K. (1999) *Nuclear Instrument & Methods in Physics Research Section B-Beam Interaction with Materials and Atoms* 151(1-4): 232-237.
7. Fischer, D.; Lappan, U.; Hopfe, I.; Eichhorn, K.J.; Lunkwitz, K. (1998) *Polymer*, *39*(3): 573-582.
8. NMT-SPEC-001, *Procurement of Arm-Length Dry Box Gloves Lead-Loaded Neoprene, Hypalon*, NMT-SPEC-005, *Procurement of Arm-Length Butyl Dry Box Gloves*, and NMT-SPEC-006, *Procurement of Hypalon Arm-Length Dry Box Gloves and Port Covers*.
9. Standard test methods for vulcanized rubber and thermoplastic elastomers-tension. Annual book of ASTM standards 09.01 (D412-98a); (1998) p 41-53.
10. Gillien, K.T.; Celina, M.; Clough, R.L.; Wise, J. (1997) *TRIP* 5(8): 250-257.
11. NMT9-HCP-010, *^{238}Pu Heat Sources, Fuel Containers, and RTGs* and NMT9-HCP-011, *Operation and Maintenance of Milliwatt RTGs and RTG Electrical Tester*.