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Urethane Elastomers: Development of TDI-Free Replacement Materials for EN-7

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Urethane Elastomers: Development of TDI-Free Replacement Materials for EN-7

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ABSTRACT

TDI-free urethane elastomer formulations with excellent electrical properties have been developed as replacements for EN-7, a commercial TDI-based elastomer used for encapsulation in many weapon applications. TDI (toluene diisocyanate) is an OSHA-regulated volatile diisocyanate and has been targeted for elimination from future weapons use. As a result of this and earlier toxicity concerns, there have been efforts over many years within the DOE complex to identify urethane materials meeting the needed performance standards while minimizing health hazards during processing.

No TDI-free commercially available formulations with electrical, mechanical and processing properties equivalent to EN-7 have been identified to date. Previous DOE programs have evaluated a variety of formulated replacements with reduced levels of free TDI although none have provided the exceptional electrical insulating properties of EN-7. The sole exception was a recent program at Y-12 which evaluated formulations using synthetic TDI-free prepolymers and found several candidates with promising electrical performance.

The goal of the Sandia/CA program reported here was to develop simple "mix and pour" formulations based on commercially available materials which were TDI-free, readily modified for different performance requirements, and which provided both electrical and mechanical properties equivalent to EN-7. Key ingredients in these formulations were polybutadiene diols, various non-TDI liquid diisocyanates, and the same cross-linker package used in EN-7, with and without the ferric acac catalyst. No prepolymer synthesis and process development was required in this approach.

Of the formulations evaluated, the one designated DK-502NC is specifically recommended as a replacement for EN-7. This uncatalyzed formulation provided improved processing potlife over the catalyzed formulations evaluated, including EN-7, while matching its electrical and mechanical performance.

NOTE: As this report neared publication, Dow chemical announced the discontinuation of Voranol 220-530, an ingredient in both EN-7 and the formulated replacements reported here. Dow was the only supplier of this material. The vendor supplying EN-7 has purchased enough of this ingredient to insure the availability of EN-7 for several years. An effort to formulate additional EN-7 replacements which are both TDI-free and also free of Voranol 220-530 will be needed in the near future.

ACKNOWLEDGEMENTS

This work clearly built upon the efforts of others who have addressed the need for EN-7/8 replacements. Particular thanks are due to Mark Wilson at Kansas City and George Dorsey at Y-12 for their stimulating discussions and collaborations. Thanks are also due to John Moore who prompted much of this material replacement effort.

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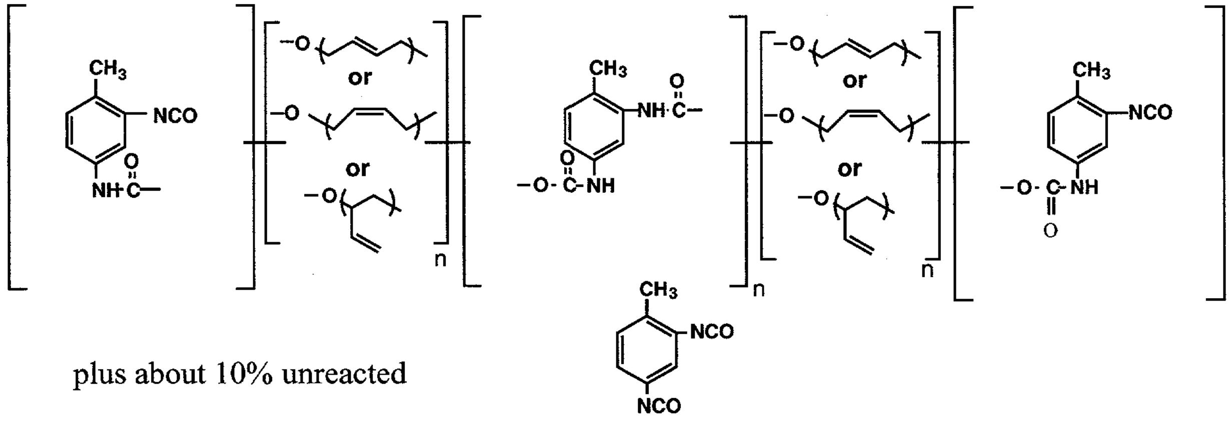
Introduction

This report describes the development of replacement formulations for EN-7 polyurethane elastomer. Key drivers behind this effort were the desire for easily processed formulations with both mechanical and electrical performance similar to EN-7 and the desire to include in the new formulations only commercially available materials requiring no pre-synthesis.

Elastomeric polyurethane encapsulants are widely used in nuclear weapons for cable, connector and transformer encapsulation. One material of choice for many years for such applications has been Conap EN-7, a commercial material based on toluene diisocyanate (TDI) and consisting of A and B components as shown below. EN-8 is identical to EN-7 except for its higher catalyst level which permits slow curing at room temperature instead of the elevated temperature cure used with EN-7.

Figure 1. Composition of EN-7 and EN-8.

EN-7/8 Part A Prepolymer: 2,4-TDI capped polybutadiene diol with about 10% unreacted TDI



plus about 10% unreacted

EN-7/8 Part B: 50/50 1,3-dihydroxy-2-ethylhexane and N,N'-(2-hydroxypropyl)aniline

plus ferric acetylacetonate (acac) accelerator (about 40 ppm in EN-7 and 250 ppm in EN-8)

Part A of these systems is sometimes sold by Conap as EN-4A since the prepolymer portion is the same for EN-4, 7 and 8. The weight mix ratio for both EN-7 and EN-8 is 100 Part A to 18.8 Part B.

A unique feature of both EN-7 and EN-8 is their exceptional volume resistivity of about $10^{15\text{-}16}$ ohm-cm at room temperature and 10^{14} ohm-cm at 200°F (93.3°C), a feature which design engineers often desire in any proposed replacement material. The reason for this exceptional dielectric performance, is the Part A prepolymer based on polybudiene polyols rather than the polyester or polyether polyols used in other urethane prepolymers. No other commercial formulations provide this level of dielectric protection while also matching the mechanical performance of EN-7/8.

The TDI isocyanate used in these formulations was designated by NIOSH in 1985 to be a suspect human carcinogen although a recent study, considered inconclusive due to its duration, found little indication of enhanced tumor formation in industrial workers[1]. Because of its high volatility, TDI was already recognized, however, as a strong lung irritant and a potential sensitizer. Individuals having or acquiring an allergic response to TDI may not be exposed to any level of TDI without exhibiting severe reactions. Engineering controls are required for any personnel working with TDI and the current ceiling PEL limit is 0.02 ppm with a TLV of 0.005 ppm. The detection limit by odor is about 10 times higher than the PEL. It should be noted that all isocyanates, volatile or not, are considered skin irritants and can cause sensitization via that route.

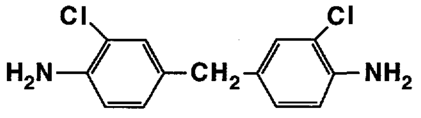
Due to these toxicity and carcinogenic concerns, a weapons complex effort was begun in the 1980s to replace TDI based urethane formulations used in elastomeric, adhesive and foam applications. A 1991 memo[2] from the Kansas City Plant to Sandia specifically requested the development of TDI-free alternatives for any production planned at that site.

The following section provides an overview of the urethane elastomers which have been used in weapon production and the previous DOE efforts to replace EN-7/8 and earlier materials. All the materials previously developed were either unable to match the electrical performance of EN-7/8, were not completely TDI-free, or required the synthesis of components which were not commercially available.

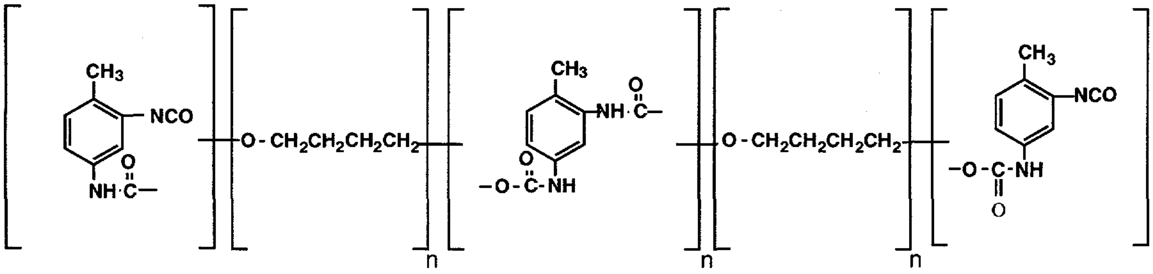
The work reported here was, therefore, initiated to develop simple TDI-free, mix-and-pour formulations based on commercially available materials and comparable in electrical, mechanical and processing performance to EN-7. The section on Formulation Strategy describes the processing requirements and other factors which constrained those commercially available materials suitable for evaluation. The Experimental and Results sections describe the work carried out and the performance of these new formulations.

Urethane Elastomers for Weapon Applications (A Brief History)

Urethane elastomers have been used as encapsulants and adhesives in weapons for decades. The material of choice until the mid-70s was often a formulation based on Adiprene L-100 and MOCA



MOCA or MBOCA: 4,4-methylenebis (2-chloroaniline)



Adiprene-L-100

Adiprene L-100 is a prepolymer of TDI and polytetramethylene oxide, a polyether diol. Because of the higher oxygen content of this and similar prepolymers, none of these systems have the extremely high electrical resistance found with the polybutadiene polyol based prepolymers used in EN-7/8. MOCA was ruled by OSHA in 1973 to be a possible human carcinogen and led to DOE efforts to identify alternative formulations even though the OSHA ruling was later overturned by court action. It was again added to the suspect carcinogen list in 1983.

Two leading candidates identified within Sandia as replacement materials were Conap's EN-7 and Hexcel's Uralite 3121S[3] (this reference provides an excellent review of urethane elastomer chemistry and the encapsulant elastomers available at that time). EN-7/8 were developed by Conap (with assistance from Sandia[4]) by replacing the toxic mercuric catalyst in their EN-4/5 products with ferric acetylacetonate (acac). EN-7, in particular, has been widely used in weapon applications since then and was noted for its exceptional dielectric properties. The load bearing and high temperature performance of EN-7 were not as high as found with Adiprene L-100/MOCA but were adequate for many applications. EN-7, because of the amine group in the Voranol 220-530 diol, is also incompatible with explosives such as HNAB. Uralite 3121S (based on a prepolymer of MDI and polytetramethylene oxide and cured with a mixture of butane diol and polytetramethylene oxide diol) was superior to EN-7 in heat resistance, was compatible with explosives, and was considered a good alternative replacement elastomer although it also contained a mercuric catalyst. Pantex has reported its evaluation as an assembly adhesive[5]. The dielectric performance was similar to the Adiprene L-100 type formulations due to the polyether backbone. This formulation has now been replaced by Hexcel 3125A/3119B but is still catalyzed by phenyl mercuric neodecanoic and N-methylpyrrolidone.

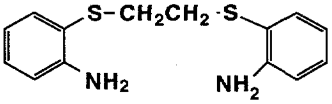
A study of the elastomer morphology, the hard and soft segments, of the Adiprene/MOCA, EN-7 and Uralite 3121-S formulations was also carried out at Sandia at that time[6]. This work indicated that a more crystalline hard segment would improve the high temperature performance of both EN-7 and 3121S. The excellent mechanical and high temperature properties of Adiprene/MOCA are due in large part to the aromatic amine curing agent (MOCA) while the replacement systems are polyol cured. The desire to replace MOCA with another aromatic amine to more fully duplicate its performance led, especially with the later need to replace EN-7 because of the TDI issue, to the use of various aromatic amines in replacement candidates, particularly Cyanacure. Work at Sandia in the late 70s had already indicated that Cyanacure, then known as Apocure-601, was a promising and less mutagenic MOCA replacement[7].

Y-12[8,9] and LLNL[10,11,12] had evaluated two additional replacements for Adiprene L-100/MOCA. Adiprene L-315 is prepared with a lower molecular weight polyether than used in L-100 with about 4% free TDI and was cured with a ferric acac catalyzed 7/2 mixture of butanediol (BD) and trimethylolpropane (TMP). Adiprene LW-520 is a prepolymer of polytetramethylene oxide and hydrogenated MDI (similar to the Halthanes described below) and was cured with methylene dianiline (MDA or Shell Z). These systems were basically suggested in DuPont's Adiprene literature and modified as required. The first system required longer cures and had a higher Tg and creep than the Adiprene/MOCA system. A similar encapsulant using Adiprene L-100 cured with an uncatalyzed BD/TMP mixture was later used at Pinellas Plant as a neutron generator encapsulant. The Adiprene LW-520/MDA system suffered from high viscosity and short potlife and also contained another aromatic amine later suspected to be carcinogenic.

A Kansas City study[13] of the hydrolytic stability of many of the proposed alternatives found EN-7 to be the most stable compared to EN-8, Uralite 3121, the other Adiprene based systems and even Adiprene/MOCA.

Additional alternatives were later developed at LLNL[14] based on new polytetramethylene oxide prepolymers of either MDI (the Halthane 73-series) or hydrogenated MDI (the Halthane 87- and 88-series using Desmodur or Hylene W). Using aromatic amine curing agents these prepolymers, prepared at Kansas City, overcame some of the temperature sensitivity problems encountered with the Adiprene L-315/diol system and improved other properties needed for certain weapon applications.

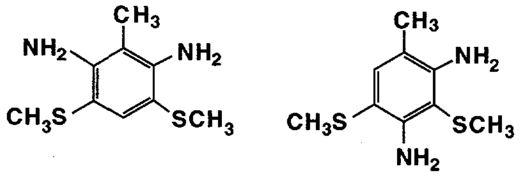
With the subsequent identification of TDI as a suspect human carcinogen, a DOE-wide effort to identify replacements for EN-7 led to the selection of Adiprene L-100 cured with Cyanacure, an aromatic amine alternative to MOCA. A thorough evaluation at Kansas City found it had similar adhesive performance to Adiprene/MOCA[15]. This diamine is also used at Kansas City to synthesize a bismaleimide used in a variety of syntactic foams for weapon applications. Cyanacure, according to its MSDS, has shown mutagenic activity in in-vitro, "short term genotoxicity" (Ames) tests but has not been listed as potential human carcinogen by OSHA or under California's Prop. 65. While



Cyanacure (known earlier as APO-Cure 601 and more recently as Versalink 138, depending on the vendor)

Adiprene L-100 (or an equivalent product RN 1501) is also a TDI prepolymer, the level of free TDI is only about 0.1% instead of the 10-12% present in EN-7/8A. Another alternative formulation used Pet 90A which has even less free TDI at about 0.05%.

When Cyanacure became commercially unavailable for several years, another diamine, Ethacure 300 was identified as an alternative curing agent. This amine also was positive in Ames tests with other toxicity tests still in progress. Cyanacure reappeared recently as a commercial product under the name Versalink 138 although the high cost of this product has prompted Kansas City to evaluate its in-house synthesis. During the work to identify a replacement for Cyanacure, a wide variety of formulations cured with alternate aromatic amines were evaluated by a working group with participants at Sandia, Kansas City, Y-12, Mound, and Los Alamos (see Appendix A). Beyond the toxicity concerns raised by aromatic amines, most are also solids and less convenient to process. Ethacure 300 and Asilamine 170 have received attention in part due to their liquid state and easy processing. Details of all those different studies have never been assembled although a list of the systems evaluated is given in Appendix B. Comparisons of the Ethacure 300 and Cyanacure curing agents with both Adiprene L-100 and PET 90A were reported by Sandia[16,17] and Kansas City[18].



Ethacure 300, a liquid blend of two isomers.

None of the above formulations based on Adiprene L-100, RN 1501 and Pet 90A showed dielectric performance equivalent to EN-7/8 since all were based on prepolymers of TDI with a polyether diol instead of the polybutadiene polyol used in EN-7/8A. The LLNL Halthane elastomer materials gave better volume resistivities than the TDI-polyether formulations but still not as good as EN-7/8.

Table 1 summarizes representative data, either from brochures or DOE complex evaluations on some of the key systems discussed above.

Visits to Conap (George Dorsey of Y-12 and Mark Wilson of Kansas City) and repeated searches for commercial products had identified no materials which appeared equivalent to EN-7/8 in <u>both</u> electrical and mechanical performance. Urethane and epoxy encapsulants from vendors such as 3M (Scotchcast Resins), Insulcast, Dexter-Hysol, Thermoset Plastics, Epoxies, Etc. (one product evaluated as part of this program) and others might provide similar dielectric protection but did not provide equivalent mechanicals, or vice-versa. The often proprietary composition of such commercial systems also precluded any protection against future formulation changes or product discontinuations, both of which are not uncommon situations.

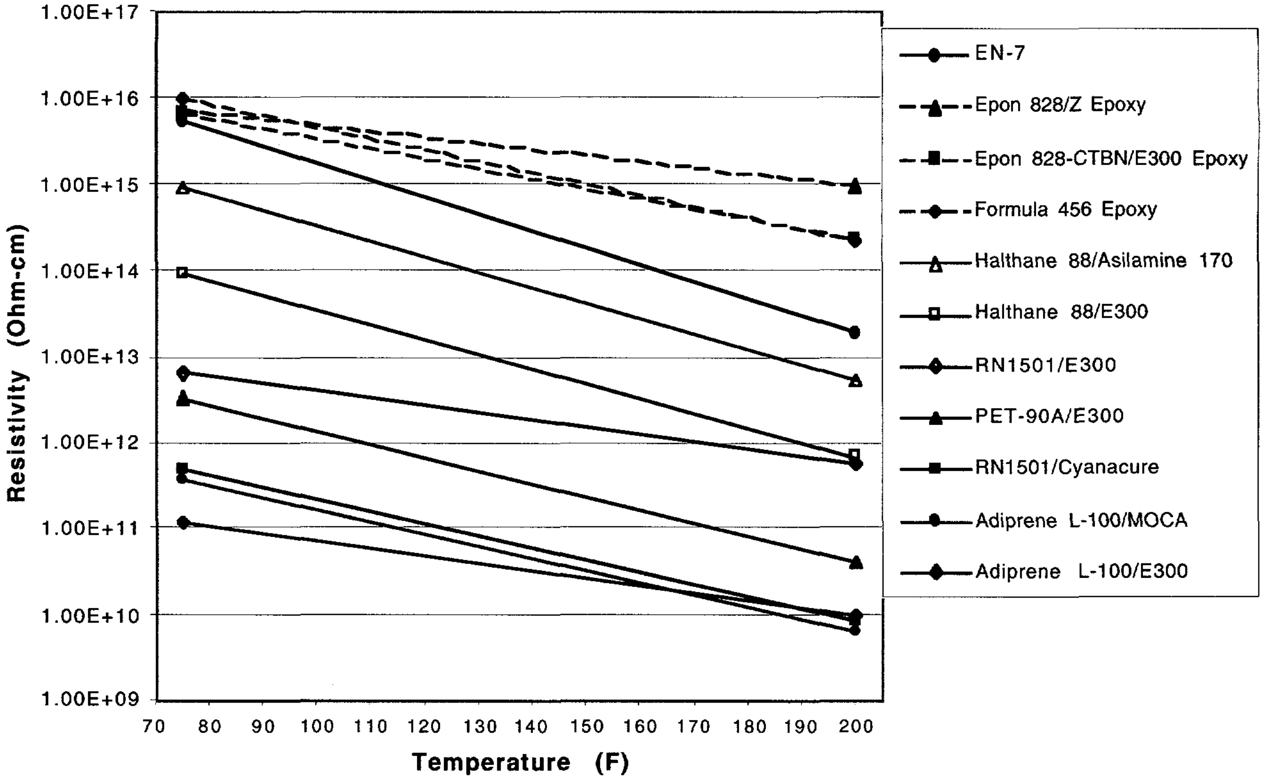
Table 1. Representative Mechanical and Electrical Properties of Key Polyurethane Elastomers

	RN 1501, MOCA	Adiprene L-100, Cyanacure	RN 1501, Ethacure 300	Pet 90A, Cyanacure	Pet 90A, Ethacure 300	EN-7	EN-8
Mixed Viscosity	(Note: Adiprene L-100 and RN 1501 are "equivalent" products.)						
at 23°C, cps						5500	5500
at 71°C, cps	5000	5000	5000	2800	2800		
NCO Content, %	4.2	4.2	4.2	3.8	3.8	9.0	9.0
Free TDI Content, %	<0.2	0.12	<0.2	0.05	0.05	~10	~10
CTE, ppm/°C	209	210	210		228	168	
Hardness, Shore A	95	95	90	92	87	90	90
Tg, °C	-44 to -36	-42	-39	-64	-64	-77	-77
Tensile Strength, psi	4571	3539	4807	3245	4363	2200	2200
Elongation, %	381	507	408	523	468	450	450
Tear Strength, ppi	420	469	447	405	435	305	305
Dielectric Strength, vpm	335	356	353	351	395	670-785	670-785
Dielectric Constant, Hz						2.8, 10^6	2.8, 10^6
Volume Resist., Ohm cm	3.3×10^{12}	3.1×10^{11}	4.9×10^{12}		4.0×10^{12}	$4.3\text{-}8.9 \times 10^{15}$	4.3×10^{15}
Dissipation Factor, Hz						0.012, 10^6	0.012, 10^6

While most applications do not require the extremely high level of electrical insulation provided by EN-7/8 it is often desired as an additional design margin. One specific application in which such high resistivity was desired in the encapsulant was the SA2404-11 connector. With that application as the target, a variety of available materials were compared to EN-7 as potential encapsulants at Kansas City[19]. Several DOE-formulated rigid epoxy encapsulants used in other weapon applications were included and did indeed have excellent insulation performance but were also clearly non-elastomeric. Volume resistivity and other tests were carried out and are shown in Figure 2 and summarized in Table 2. The only materials as good or better than EN-7 in volume resistivity were the non-elastomeric epoxy encapsulants. The closest urethane candidate was, surprisingly, Halthane 88 cured with Asilamine 170, both of which are non-commercial materials requiring synthesis at Kansas City. The adhesion of this formulation was marginal as was its processing potlife, however, and it was not further evaluated.

In order to provide a more complete alternative to EN-7/8 a program was begun at Y-12 by George Dorsey to synthesize and evaluate TDI-free prepolymers based on polybutadiene polyols. Materials developed at Y-12 have been evaluated at Kansas City where volume resistivity and cable application results confirmed the excellent dielectric performance of such polybutadiene-based systems.

Figure 2. Volume Resistivity of Potential Connector Encapsulants.



A companion program was later begun in 1997 at Sandia/CA to develop formulations which did not require an intermediate synthetic step to make such prepolymers and comprises the work reported here. During the initial planning for this program, a review of brochures produced by Elf Atochem[20], the producer of the polybutadiene polyols, found a suggested series of simple mix-and-pour formulations using their polyols and requiring no prepolymer synthesis. Many of these were filled or heavily plasticized with cable oils, but one formulation was similar to EN-7 in overall performance and served as a starting point for the work here.

A 1996 publication[21] also described urethane elastomers based on Amoco's DIFOL line of polybutadiene diols which are similar to the Elf Atochem products except for the absence of 1,2 polybutadiene units giving a linear structure and functionality of two. That report describes TDI prepolymers similar to that in EN-7/8 and cured with MOCA and also mix and pour formulations based on butadiene diols, a low molecular weight diol (either butanediol or Voranol 220-530), and melted MDI. The DIFOL diol product line has not been commercialized, however, and DIFOL-based formulations were not evaluated here. An additional source of the polybutadiene raw materials, Kaucuk, a.s., in the Czech Republic, was recently identified although their products (known as Krasol) were not evaluated. Their literature[22] does suggest the use of the hydroxyl terminated Krasol LBH in urethane formulations and they also market a TDI prepolymer, Krasol LBD, which may be similar to the prepolymer used in EN-7.

Table 2. 1996/7 AlliedSignal/FM&T Evaluations of EN-7 and Alternative Connector Encapsulants

		EN-7	**H88/A170**	**H88/E300**	**PET 90A/E300**	**Formula 456 Epoxy**
PROCESSING	Mat l State at RT (Base/Curing Agent)	liquid/liquid	solid/liquid	solid/liquid	solid/liquid	liquid/liquid
	Mix Ratio (pbw)	100 Part A 18.8 Part B	100 H88 19.7 A170	100 H88 12.3 E300	100 PET 90A 9.2 E300	50 DER 330 25 XU-71790 12.5 Jeff. D230 12.5 Anca.2049
	Cure Schedule	16 hrs @ 160¡F	16 hrs @ 160¡F	16 hrs @ 160¡F	16 hrs @ 160¡F	4 hrs @ 200¡F + 16 hrs @ 260¡F
	Viscosity (cps x 1000) (initial/10 min/15 min) at					
	Rt		18/20/30	3/3.5/4.5	8.3/8.5/9.8	
	120¡F		8/14/>30			0.25
	140¡F		6/>30/>30		3/4.5/18	0.115
	160¡F		5/>30/>30	4/3/4	3/12/>30	
MECHANICAL	Tensile Strength (psi)	1935	5060	2480	4363	8870
	Elongation (%)	440	550	806	468	5-10
	100% Modulus	885	1320	620	1062	not applicable
	200% Modulus	1090	1690	780	1322	
	300% Modulus	1325	2340	970	1641	
	Hardness (Shore A)	94	98	85	87	
	Tear Strength (pli)	295	480	340	435	
	Shear Storage Mod. (psi)					
	@ ˚25¡C		8000	3000	2000	
	@ 100¡C		5800	1800	3000	
	@ 125¡F		4700	1700	4500	
	T-peel strength (pli): Nylon/Kapton	9.9	10 (1 sample)	32.6 (1 sample)	10.6	
	wet-blast aluminum (days aging at 60¡C)	26.5 (36) 27.5 (136)	16.4 (13) 10.2 (117)	39.9 (14) 12.0 (137)	6.0 (15) 6.3 (35)	
THERMAL	Tg (¡C)	-77	-72	-67	-64	95-110
	Heat Deflect. Temp. (¡F)		380	330	330	
	CTE (ppm/¡C)					
	—53 to 23	168	194	191	226	69
	23 to 74		188	182	230	80
ELECTRICAL	Dielectric Constant	2.64	4.63	5.22	4.40	3.96
	Dissipation Factor	0.008	0.016	0.025	0.026	0.009
	Volume Resistivity (ohm-cm)					
	@ RT	5.61 E15	9.54 E14	9.70 E13	3.28 E12	--
		1.92 E13	5.41 E12	6.95 E11	4.04 E10	2.27 E14
	Dielectric Strength (V/mil)	670	405	383	389	631
	Connector Insulation Resistance (ohms)					
	@ RT	1.04 E13	2.18 E13	2.01 E13	9.44 E11	2.30 E13
	@ 165¡F		3.42 E12	7.96 E11		1.23 E13
	@ 200¡F		8.72 E11	2.77 E11	6.20 E9	1.88 E12

All data compiled by Greg Manke (AlliedSignal/FM&T, March 19, 1997)

Formulation Strategy

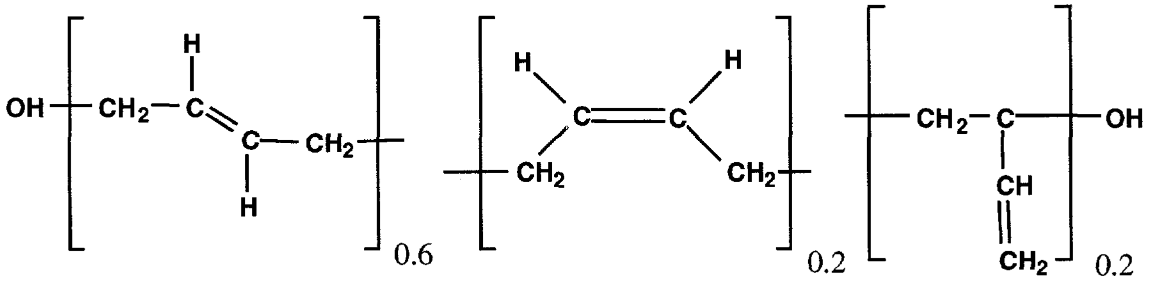
Required formulation components were a high equivalent weight polyol to impart flexibility, a low equivalent weight polyol to provide rigidity, and a diisocyanate to react with both to form urethane linkages. No formulations using aromatic amine cross-linkers such as used in prior DOE studies were evaluated due to concerns over toxicity, processability and availability.

Previous results indicated that the high molecular weight polyols used in the formulations must be based on polybutadiene in order to match the electrical performance of EN-7. The unique commercial status of the EN-7 and 8 products results from the absence of other commercial isocyanate prepolymers which use those polyols in place of the standard polyether and polyester diols and polyols. Both the polyethers and polyesters are more oxygenated and more polar than the hydrocarbon based polybutadienes. Prepolymers of TDI and such polybutadiene polyol are made by Conap for captive use. No manufacturers of polybutadiene prepolymers based on isocyanates other than TDI were identified, resulting in the synthetic work at Y-12 discussed previously.

The polybutadiene polyol raw materials from Elf Atochem (previously Arco) have the composition shown in Fig. 3 and are available in two molecular weights (Mn), 1400 and 2800. Their standard product is R-45HT having a molecular weight of 2800 and functionality of 2.5-2.6. It was upgraded to R-45HTLO in early 1998 when process changes were implemented to reduce the level of residual cyclooctatetraene and therefore the odor of the product (LO = low odor). These products are not pure diols due to branching during the polybutadiene polymerization although a more linear, and more expensive, product R-45M (functionality 2.1) is produced in limited quantities. This material would probably be similar to the uncommercialized BP/Amoco DIFOL diols discussed above. All the new formulations evaluated here were based on the standard R-45HTLO product as were the formulations suggested by the Elf Atochem literature.

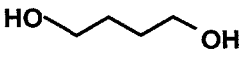
A variety of low molecular weight polyols are available and those commonly used in urethane elastomers are shown in Figure 4. Two of these are used as a 50/50 mixture in the Part B component of EN-7/8. 1,3-dihydroxy-2-ethylhexane is a clear, low viscosity liquid. N,N'-(2-hydroxypropyl)aniline is a low melting solid and has been sold as Isonol 100 and, more recently, Voranol 220-530. Both of these diols are more compatible than butane diol or trimethylol propane with the polybutadiene polyols due to their higher hydrocarbon content and were presumably chosen by Conap for that reason. The amine groups in the Voranol diol are also believed to enhance mechanical performance due to hydrogen bonding. The reported work with DIFOL butadiene diols also noted better properties when the elastomers were cured with Voranol 220-530 than with butane diol and attributed the performance to better compatibility[21]. The EN-7B diol mixture is liquid and more convenient to use than pure Voranol 220-530 and contains a pre-blended ferric acac catalyst to enhance reactivity. To maximize convenience and match the composition of EN-7 as closely as possible, it was decided to simply use the Part B component of EN-7 as the cross-linker/catalyst package in the majority of the new formulations. As noted in a later section on potlife, elimination of the EN-7B ferric acac catalyst and use of a simple diol blend of 1,3-dihydroxy-2-ethylhexane and Voranol 220-530 significantly improved the processing potlife of such formulations. The diol blend also eliminated any inconvenience associated with the use of pure Voranol 220-530 which tends to solidify at room temperature.

Figure 3. Structure of Polybutadiene Polyol.

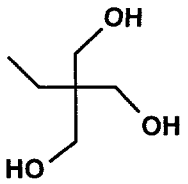


Most polybutadiene diols contain a 6/2/2 ratio of trans, cis and vinyl (1,2) isomers. While shown as a linear diol, the Poly bd R45HTLO polyol actually has a functionality of about 2.5-2.6 due to branching through the 1,2-butadiene units. The DIFOL diols reported but not commercialized by BP/Amoco contain no 1,2-butadiene units and are true diols.

Figure 4. Structures of Low Molecular Weight Diols/Triols.

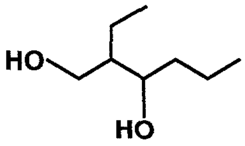


butane diol
functionality = 2
MW = 90 (45 gr/OH)



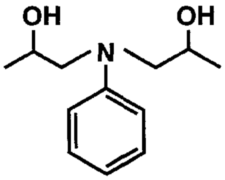
trimethylol propane
functionality = 3
MW = 134 (45 gr/OH)

2-ethyl-1,3-hexanediol (EHD)



functionality = 2
MW = 146 (73 gr/OH)

N,N'-(2-hydroxypropyl)aniline



functionality = 2
MW = 209 (105 gr/OH)
Voranol 220-530

EN-7B contains a 50/50 mixture of EHD and Voranol 220-530 plus ferric acac catalyst.

Because no prepolymer synthesis was desired, the isocyanate portion of the formulation was restricted to commercially available diisocyanates which were liquid at room temperature. The variety of both aromatic and aliphatic isocyanates available is shown in Figure 5. Many of the commercially available materials are based on quasi-prepolymers of methylene diphenylisocyanate (MDI) which is normally a solid but can be readily liquefied by partial pre-reaction with either itself or a diol such as ethylene glycol or diethylene glycol. The exact composition of many of these products is proprietary. A more recent approach to liquefying MDI has been the use of mixtures of the standard 2,6 isomer plus the 2,4 isomer. This is the basis for Isonate 50 and, apparently, also Rubinate 9225 and 9258. Rubinate 9225 is specifically sold as a "TDI replacement".

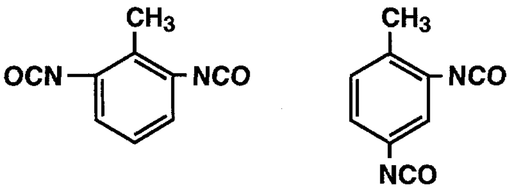
To retain similarity to EN-7/8, particularly in radiation resistance, only aromatic isocyanates were used in the new formulations. The five selected were Rubinate 1680, Rubinate 9225 and Rubinate 9258 from ICI and Isonate 50 and Isonate 2181 from Dow. All are low viscosity products with functionalities ranging from 2.0 to 2.3. Some preliminary work was also carried out with TMXDI from Cytec although the extremely slow cure rate of this diisocyanate led to its elimination from the study. Table 3 summarizes key parameters for all the isocyanate and polyol materials used.

A variety of mix-and-pour formulations shown in an Elf Atochem brochure[20] on the use of Polybd resins in electrical applications all showed excellent volume resistivity values and these are shown in Table 4. Tg values were not provided. Of the formulations shown, Formula "B" was chosen as a baseline due to its close similarity to the performance of EN-7. The extremely short potlife of the tin catalyzed formulation was confirmed and that catalyst was replaced with ferric acac, the same catalyst used in EN-7. In this case the ferric acac was predissolved in the Polybd. Lead octoate, used in most of the Elf Atochem formulations, was avoided for toxicity concerns. The diisocyanate used in this formulation, Isonate 2143L, was also considered problematic due to unpublished Sandia results showing the evolution of phosphoric acid from foams based on this material during heat aging. The phosphoric acid was generated from the phosphate ester used as a catalyst during manufacturing. A replacement diisocyanate, Rubinate 1680, uses a phosphine oxide catalyst which does not generate acid residues. The use of Voranol 220-530 as the only diol, as shown in these formulations and discussed above, was less convenient to process than EN-7B due to the need to melt the material.

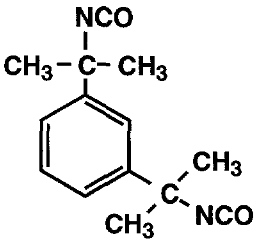
Using the materials selected in Table 3 below and a general approach similar to that suggested by Elf Atochem, a series of urethane elastomer formulations were defined and evaluated using EN-7 and the Elf Atochem "B" formulation as controls. Those experimental procedures and results are described below. No attempt was made within this program to formulate an elastomeric epoxy encapsulant since the target requirements were readily met with urethane formulations which closely duplicated the EN-7 performance in all tests performed. The excellent electrical performance seen with existing epoxy encapsulants in the Kansas City tests might partially reflect the rigidity of those materials, and the limited number of epoxy resins and curing agents with high flexibility and low oxygen content also constrained the epoxy formulation options available.

Figure 5. Commercial Diisocyanates.

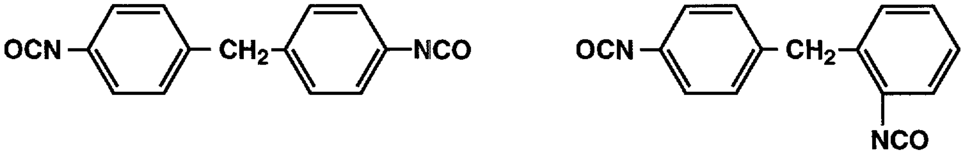
Aromatic Diisocyanates:



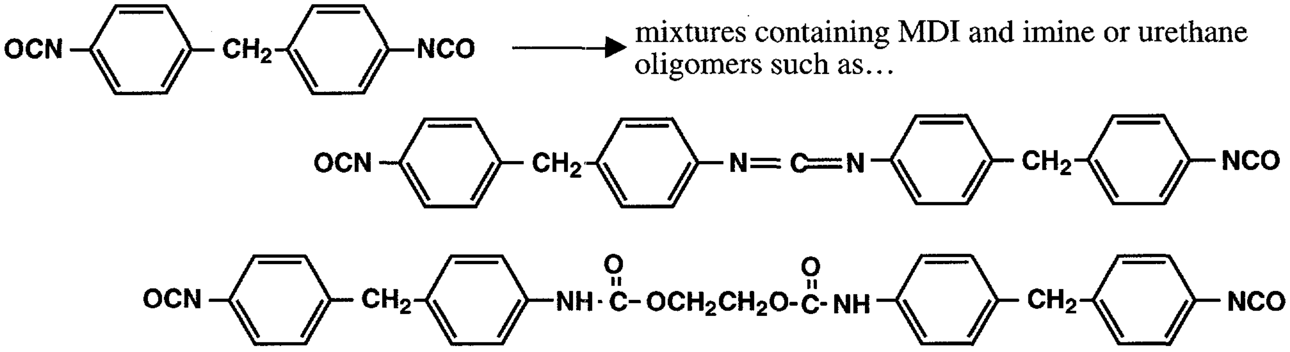
TDI, mixture of 2,4- and 2,6- isomers, usually pre-reacted with a high MW diol to form a prepolymer such as Adiprene L-100 or RN 1501.



m-TMXDI (Elf Atochem), MW = 244.3
Meta isomer is liquid, para isomer is solid.
Combination aromatic/aliphatic character.



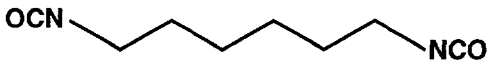
Isonate 50 (Dow), 50/50 liquid blend of 2,4 and 2,6 MDI isomers. Rubinate 9225 and 9258 also contain the 2,4 isomer to liquefy the MDI blend although the level is not specified.



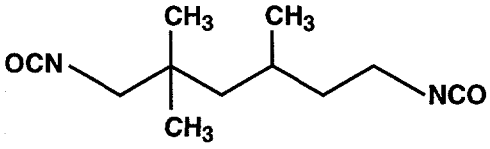
mixtures containing MDI and imine or urethane oligomers such as...

MDI, solid unless modified by partial dimerization and dehydration to imine (Isonate 143L/2143L or Rubinate 1680) or partial pre-reaction with ethylene glycol (Isonate 181/2181) or other polyols.

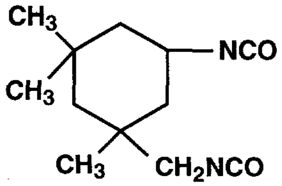
Aliphatic Diisocyanates:



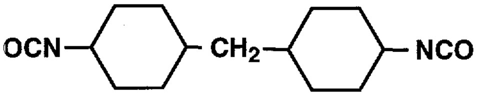
HMDI (hexamethylene diisocyanate)



TMDI (trimethylhexamethylene diisocyanate)



IPDI (isophorone diisocyanate)



H12 MDI (Desmodur W, Bayer)

Table 3. Formulation Ingredients (see preceding figures for structures)

Component	Vendor	Molecular Weight (Mn)	Function-ality	Weight per OH or NCO	Viscosity (cps)
Polybutadiene polyols:					
R-45HTLO	Elf Atochem	2800	2.5-2.6	1180	8000 at 23°C 5000 at 30°C
Cross-linkers:					
ethylhexanediol		146	2.0	73	low
Voranol 220-530	Dow	209	2.0	105	solid
EN-7B (50/50 blend of DEH and Voranol 220-530)	Conap	--	2.0	86	850±250
Isocyanates:					
Isonate 2143L	Dow	305	2.1	145	40
Isonate 50	Dow	250	2.0	125	10
Isonate 2181	Dow	366	2.0	183	770
Rubinate 1680	ICI	300	2.1	143	40
Rubinate 9225	ICI	284	2.1	135	30
Rubinate 9258	ICI	304	2.3	132	40
TMXDI	Cytec	244	2.0	122	10
2,4-TDI (for comparison)		174	2.0	87	low (mp 20-22°C)

Table 4. Vendor Suggested Formulations (from Atochem Poly BD resins brochures*

Formulation Ingredients	EN-7/8	T2(5)	T4	T5 / "A"	"B"	T6	T7	T8
Part A:	Conap lit.					Plasticizer and clay modified		
Poly bd R-45HT		100.00	100.00	100.00	100.00	100.00	100.00	100.00
Voranol 220-530 (PDIPOA)		11.85	6.30	17.15	17.15	8.58	17.15	8.58
Cyanox 2246 antioxidant		0.10	1.00	0.10	0.10	1.00	1.00	1.00
T-12 catalyst (dibutyl tin dilaurate)		4 drops			0.05			
Lead Octoate soln (24% Pb)			0.05	0.05		0.07	0.20	0.07
Foamkill 8D			0.05			0.05		
Diundecyl Phthalate plasticiser								52.7
Cable Oil 750-45 plasticiser						52.7	80.00	
Burgress KE clay							80.00	
Total (organics only)		112.00	107.40	117.30	117.30	162.35	198.35	162.35
Part B:								
Isonate 2143L (formerly 143L)		29.78		37.19	37.19		37.19	
PAPI 901			19.30					
Properties:								
Mondur MR22.9722.97								
10^{16}—$7.1x10^{15}$ $1.2x10^{16}$ $1.9x10^{16}$ $9.0x10^{15}$								
$1.3x10^{15}$ $1.9x10^{14}$ surface resistivity, ohm								
(ASTMD-257—$\geq 2.0x10^{17}$ $9.5x10^{16}$								
$\geq 2.8x10^{16} \geq 1.4x10^{17} \geq 1.4x10^{17}$								
volume resistivity, ohm-cm (ASTM D-257)10^{15}	$\geq 1.4x10^{17}$							
dielectric strength, volts/mil (ASTM D-149)	670-785	--	305	622	574	609	641	548
dielectric constant, 10^6 Hz (ASTM D-150)	2.8	--	3.06	2.90	2.78	2.81	2.86	3.66
dissipation factor, 1 kHz (ASTM D-150)	0.012	--	0.0268	0.0170	0.0143	0.0156	0.0128	0.0202
embedment stress @ -40°C, psi	--	--	360	360	--	0	0	0
hardness, Shore A	90	82	56	82	84	48	63	47
Naval Avionics Hard. Aging (28 d, 100°C, 95% RH)		--	50 to 48	81 to 81	--	42 to 43	65 to 68	42 to 42
Tensile strength, psi	2200	1192	368	1174/1774	1770	266	908	185
elongation	450	245	170	207	270	125	207	95
100% modulus, psi	--	465	255	868	980	206	538	185
tear strength, Die C, pli	305	150	63	149	--	24	76	19
pot life, min. to reach 100,000 cps	--	--	45	19.5	4.9	73	32	83

* Formulations "A" and "B" were described in a one-page supplement to the electrical applications brochure and compared two different catalysts (lead octoate and dibutyltin dilaurate) in the same formulation. Formula "A" had appeared as T5 in the original brochure. Replacement of the lead octoate catalyst with a tin catalyst had a major effect on the potlife but no significant effect on properties. Table 2 in the brochure had compared different ratios of Poly bd and Voranol 220-530 and Example 5 with the hardness closest to EN-7 was selected and shown as T2(5).

Both one stage (mix and pour) and two stage (separate prepolymer synthesis) formulations are widely used in cast elastomers. Possible differences between the two techniques include the casting exotherms with large batches, the A/B processing ratios for machine mixed materials, and overall formulation compatibility. Elastomeric urethanes typically have both "hard (rigid)" and "soft (flexible)" segments which are incompatible following cure. This hard/soft phase morphology provides the desired rubbery properties as well as crosslinking to avoid a leathery or cheesy product with no mechanical strength. Crosslinking can also be provided either by functionalities greater than 2 (as in the R45HTLO butadiene polyol and most of the isocyanates used) or by hydrogen bonding between urethane groups (a major contributor to urethane performance) as well as the physical segregation of rigid domains. Opacity varies with the initial compatibility of the reactants and with the developing size of the final hard and soft domains. Both the reactants used and the processing conditions can affect this phase segregation process and poor initial compatibility can lead to low molecular weights or poor uniformity. One potential advantage of synthesizing prepolymers is the control gained over the reaction of the diisocyanate with coreactants of differing solubility. The all-polyol formulations evaluated here, as noted earlier, do not have the crystalline hard phases and superior heat resistance of the aromatic amine cured formulations. All the mix-and-pour formulations did show opacity early in the reaction and were opaque following cure. They were more opaque than the control EN-7 castings and similar to the Elf Atochem castings. The level of incompatibility during reaction and evolution of the phase separation were noted but not investigated since the final casting appearance and mechanical properties did not indicate any significant problems with incompatibility or casting inhomogeneity. The similar reactivity of the butadiene polyols and EN-7B diols plus the initial compatibility of those reactants probably mitigate the potential incompatibility of the butadiene polyols and the isocyanate portion. A 1999 patent[23] describes the use of dimer diols as chain extenders because of their compatibility with butadiene polyol based isocyanate prepolymers. The dimer diol also increased the compatibility of lower molecular weight chain extenders such as butane diol and 2-ethyl-2-butyl-1,3-propanediol and allowed higher percentages of the chain extender to be used without property deterioration in the final cured part.

The mechanical performance of the castings evaluated here was used as an indicator of any undesirable phase separation or insolubility and was comparable to the prepolymer based elastomers. Further investigation of the formulation and final cured phase morphology would be of interest for future work. More detailed discussions of urethane elastomer compositions and morphology can be found in a variety of texts and handbooks[24,25,26].

Experimental

Large 14 x 15 x 1/8 inch castings weighing about 450 grams were made of each formulation. Batch sizes of roughly 500-600 grams were weighed into a small plastic tub, mixed one minute with a 4 inch Conn blade on an overhead stirrer and then degassed to less than 100 millitorr. The molds were Teflon coated steel with 1/8 inch spacers on two opposing edges and aluminum tape dams on the other two edges. They were preheated in an 80°C oven and used soon after removal from the oven. The degassed formulation was slowly poured in the center of the flat mold, taking care to minimize air entrapment, and allowed to spread. The cover plate was then laid down starting at one edge and the excess material squeezed over the mold edges on the two sides sealed with aluminum tape. After sitting at room temperature until the material was gelled, the mold was transferred back to the 80°C oven and held at that temperature for 16 hours.

Samples were cut from the casting using appropriate dies for tensile (ASTM D412 using 4.5 x 1 inch with 0.25 inch neck samples), tear strength (ASTM D624 with Die C) and hardness (Shore A with stacks of four 1-inch diameter disks) testing. Large 6 x 6 inch squares were cut for dielectric testing and small samples were also cut for thermal analysis.

The apparatus and procedures used for the electrical tests are described in Appendix C. Samples were tested as is and were not conditioned at low humidity. For tests carried out at 200°F (93.3°C), the electrode/sample/electrode assembly was preheated 2 hours. Preliminary tests with thermocouples indicated that about 1.5 hours was required to insure the sample had reached temperature. Dielectric strength measurements were carried out at AlliedSignal/FM&T. Due to a breakdown in the test equipment, data was not obtained for all the formulations. Samples for connector tests were encapsulated at Sandia and tested at AlliedSignal.

Lap shear specimens (ASTM D1002) were prepared in multiples of five from standard 2024 aluminum pieces (0.063 x 4 x 1 inch) which were machine sanded and rinsed with acetone. The pieces were overlapped (0.5 inch) in a fixturing device, the excess resin was wiped clean and the pieces clamped with two No. 50 binder clips. The bond thickness was not controlled. The clamped specimens were cured 16 hours at 80°C and aged under ambient conditions at least two weeks before testing.

Results

Formulation Screening

The first series of formulations evaluated used the ingredients shown in Table 5. All the formulations used a NCO/OH ratio of about 1.04 and were similar in design to those suggested by Elf Atochem. No antioxidant was included in this initial series. Control formulations were made with EN-7 using the same molds and procedures. The Elf Atochem "B" formulations were evaluated using both Isonate 2143L and the triethylphosphate free Rubinate 1680.

All the formulations evaluated here contained several drops of Shin-Etsu KF-865 silicone fluid (amine functionalized) to enhance degassing. This processing aid was initially identified at Sandia for use in epoxy formulations and is also effective in many urethanes. The decreased degassing time provides a longer process window before the formulation becomes too high in viscosity. Numerous tests here and at Y-12 have shown no effect on adhesive performance at the levels used in this study.

Figures 6 and 7 depict the volume resistivity and mechanical property test results using these formulations. Volume resistivities at both room temperature and at 200°F (93.3°C) were similar to EN-7. All the formulations also had similar Tg, dielectric constant, and dissipation factor values.

The tensile and tear properties of this first series, the "XX1" series, of formulations were significantly lower than observed with EN-7, however. This suggested a lower crosslink density.

Table 5. EN-7 Replacement Formulations – First Series and Controls

	EN-7	Atochem	Based	Recipes	Sandia	Mix	and	Pour	Recipes
Formulation Ingredients	EN-7	Ato "B"	"B"-143L	"B"-1680	DK-251	DK-501	DK-581	DK-801	DK-811
EN-7 Part A	100								
Diols/Polyols:									
EN-7 Part B	18.8				13.9	13.9	13.9	13.9	13.9
Polybd R-45HTLO		100	100	100	100	100	100	100	100
Voranol 220-530		17.15	17.15	17.15					
KF-865 degassing aid	trace	trace	trace	trace	trace	trace	trace	trace	trace
ferric acac (predissolved in Polybd)			0.01	0.01					
T-12 liquid (dibutyl tin dilaurate)		0.05							
Total Polyol Portion		117.2	117.16	117.16	113.9	113.9	113.9	113.9	113.9
Isocyanates:									
Isonate 2143L (formerly 143L)		37.2	37.2						
Rubinate 9225					34.7				
Isonate 50						32.1			
Rubinate 9258							33.9		
Rubinate 1680				37.2				36.8	
Isonate 2181									47.0

All DK-XX1 formulations contained 8.6-9.5% EN-7B by weight and provided a 1-1.04 ratio of NCO/OH groups.
Batches sizes mixed, in grams, were 4-5 times the parts by weight shown in the table.
Molds were preheated to 80°C but had cooled slightly before pouring.
All formulations were cured 16 hours at 80°C after sitting at room temperature long enough to gel.

Figure 6. Volume Resistivity for First Series of Formulated Urethane Elastomers (Ohm-cm at 1 KV/1 min.).

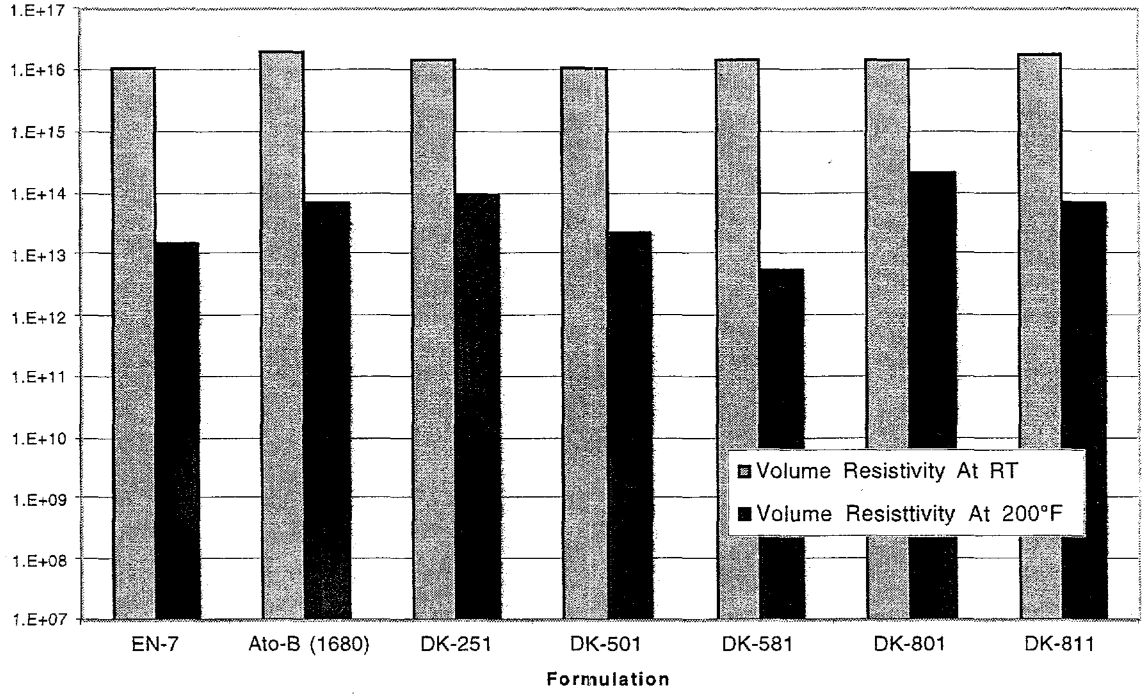
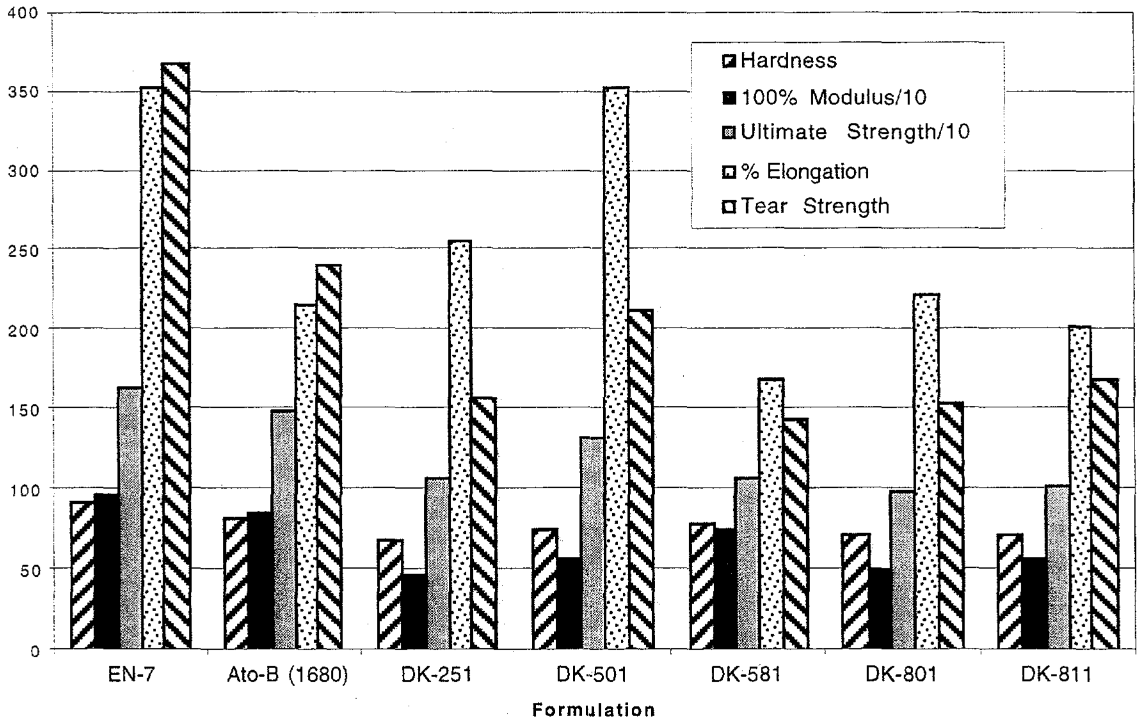


Figure 7. Mechanical Properties for First Series of Formulated Urethane Elastomers.



When the weight percent of the EN-7B component is compared, the new formulations typically contained about nine weight percent vs. almost sixteen weight percent in EN-7.

A second series of formulations was defined in which part of the Polybd polyol was replaced by a higher proportion of EN-7B while the NCO/OH ratio was kept the same. The weight percent of EN-7B in this XX2 series was 12-13%. The weight percent of Polybd decreased from about 62-68% to about 53-60% and the weight percent of the isocyanate portion increased from about 22-29% to about 27-35%. Both the first and second series of formulations are shown in Table 6 as well as two additional formulations, DK-503/4, which are discussed later. This table also shows the compositions in weight percents to allow direct comparisons.

Test results from the second series of formulations showed no change in the electrical performance but a significant overall improvement in the mechanical performance. These results are shown in Figures 8 and 9 and detailed in Table 7.

Within the XX2 series, the DK-502 formulation based on Isonate 50 showed significantly higher tear strength than the other formulations and was the only one to show values similar to those obtained for EN-7. (The DK-501 formulation also showed the highest tear strength within the XX1 formulation series.) None of the formulations showed tensile elongation values as high as the 350% found with EN-7, although the 200+% elongation shown by DK-502 would not be approached under any reasonable encapsulant or adhesive application. The hardness of DK-502 was 4-5 Shore A points lower than that of EN-7 although that is not considered a significant difference.

For comparison, two commercial urethane elastomers were also evaluated for both electrical and mechanical performance and several Sandia-formulated epoxy encapsulants were evaluated for electrical performance. The urethanes tested were Hexcel's Uralite 3125A/3119B, a polyether based formulation used in stockpile, and the recently introduced 20-2350 urethane from Epoxies, Etc[27]. The compositions of the four epoxies are shown below in Table 8. One of these is a deliberately "misformulated" version of Epon 828/Versamid 140 (referred to as Reverse Ratio Epon/Versamid) designed to provide an elastomeric epoxy encapsulant and is actually used in stockpile.

Results from these evaluations are shown in Figures 10 and 11 where they are compared to the formulations developed here and to EN-7. Both the Uralite and Reverse Ratio (RR) encapsulants showed poor volume resistivity at 200°F (93.3°C), particularly the RR epoxy. The other epoxies as well as the urethane from Epoxies, Etc. material showed excellent electrical performance. The mechanical performance of the epoxies was not evaluated as most were rigid, non-elastomeric formulations. The Uralite urethane showed superior mechanical properties, as expected. The Epoxies, Etc. urethane formulation was very soft, as indicated by the vendor, and had poor mechanical results.

Table 6. EN-7 Replacement Formulations – All Formulations

	XX1 Formula Series					XX2 Formula Series					XX3	XX4
Formulation Ingredients	DK-251	DK-501	DK-581	DK-801	DK-811	DK-252	DK-502	DK-582	DK-802	DK-812	DK-503	DK-504
Diols/Polyols:												
EN-7 Part B	13.9	13.9	13.9	13.9	13.9	16	16	16	16	16	16.5	17
Polybd R-45HTLO	100	100	100	100	100	72	72	72	72	72	65	58
KF-865 degassing aid	trace	trace	trace	trace	trace	trace	trace	trace	trace	trace	trace	trace
Cyanox 2246 antioxidant*						0.1	0.1	0.1	0.1	0.1		
Total Polyol Portion	113.9	113.9	113.9	113.9	113.9	88.1	88.1	88.1	88.1	88.1		
Isocyanates:												
Rubinate 9225	34.7					34.7						
Isonate 50		32.1					32.1				32.1	32.1
Rubinate 9258			33.9					33.9				
Rubinate 1680				36.8					36.8			
Isonate 2181					47.0					47.0		
Weight Percents:												
EN-7B	9.4	9.5	9.4	9.2	8.6	13.0	13.3	13.1	12.8	11.8	14.5	15.9
Polybd R-45HTLO	67.3	68.5	67.7	66.4	62.2	58.6	59.9	59.0	57.6	53.3	57.2	54.2
Isocyanate	23.4	22.0	22.9	24.4	29.2	28.3	26.7	27.8	29.5	34.8	28.3	30.0

* Antioxidant was added to the repeat castings of the XX2 Series and was predissolved in the combined Polybd/EN-7B polyols.

All formulations provided a 1-1.04 ratio of NCO/OH groups

Batches sizes mixed, in grams, were 4-5 times the parts by weight shown in the table.

Molds were either preheated to 54°C (XX2 Series) or preheated to 80°C and cooled slightly (XX1 Series) before pouring.

All formulations were cured 16 hours at 80°C after sitting at room temperature long enough to gel.

Figure 8. Volume Resistively for Formulated Urethane Elastomers (Ohm-cm at 1 KV/1 min.).

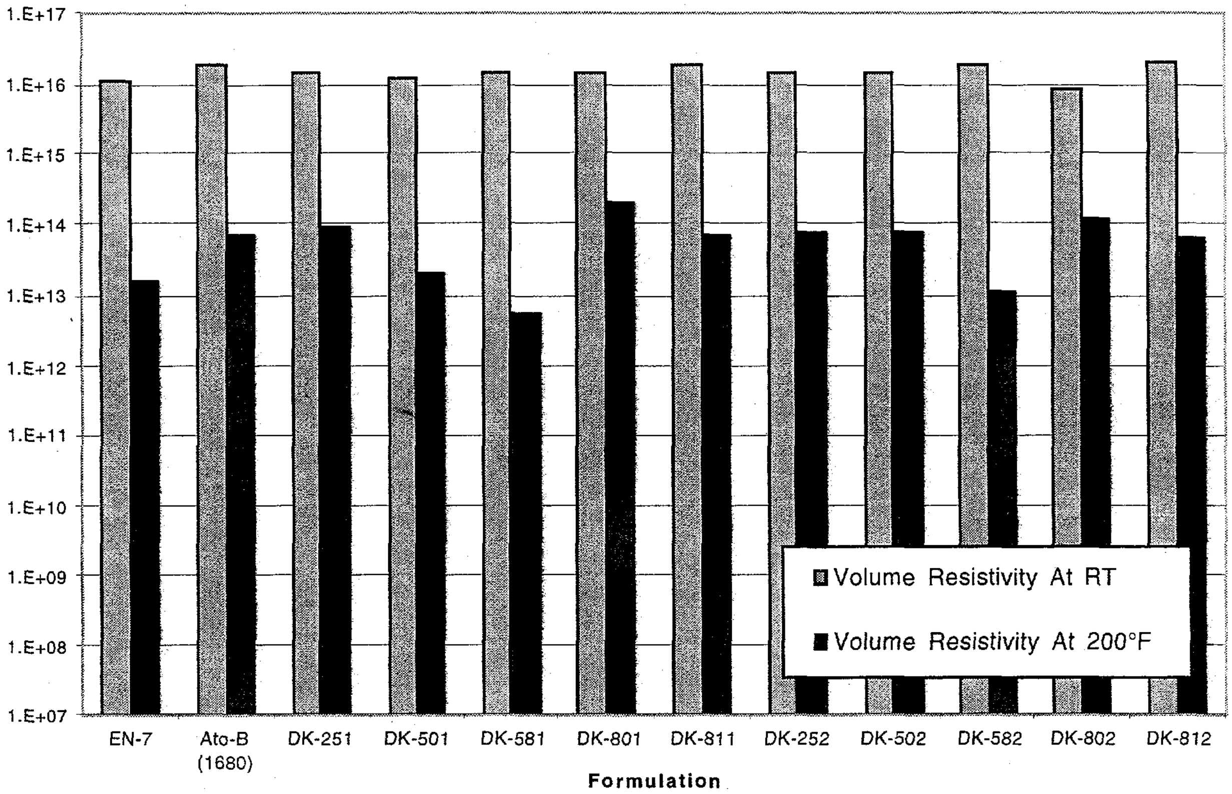


Figure 9. Mechanical Properties for Formulated Urethane Elastomers.

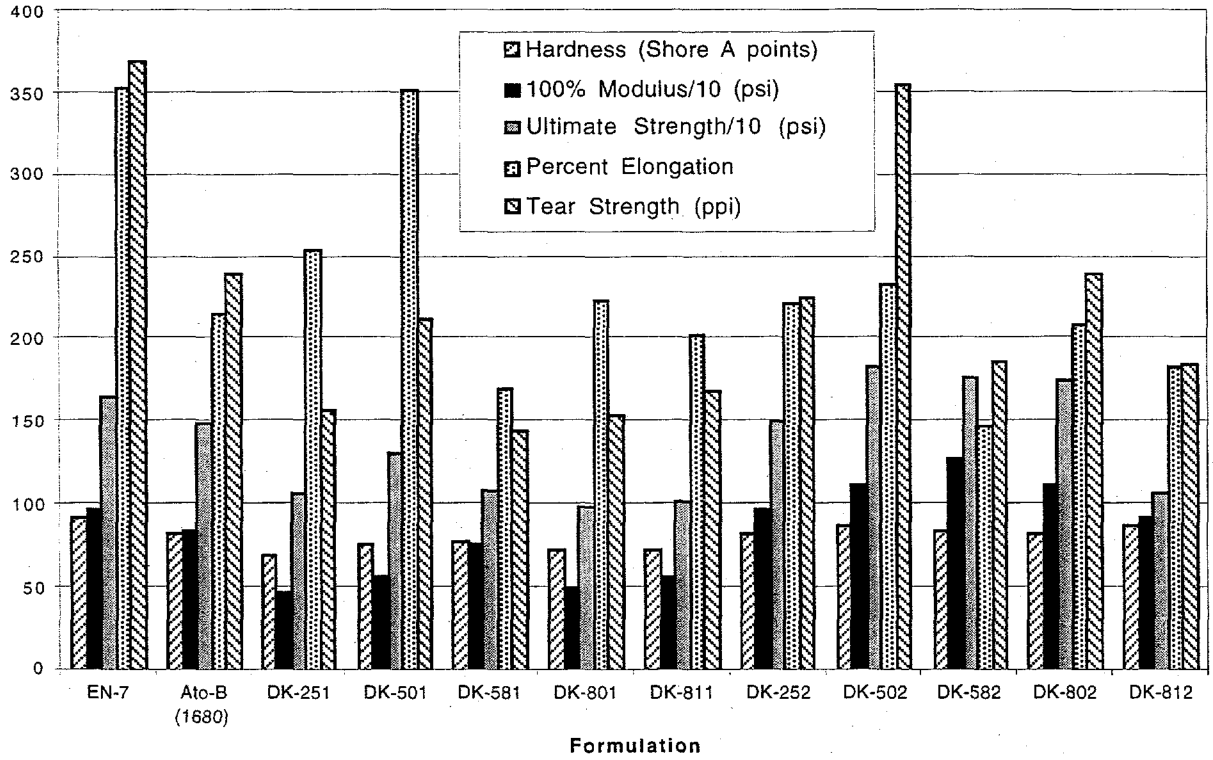


Table 7. Electrical, Thermal and Mechanical Performance of EN-7 Replacement Formulations – First and Second Series

Material	EN-7		XX1	Formula	Series		XX1		XX2	Formula	Series		XX2
	control	DK-251	DK-501	DK-581	DK-801	DK-811	Avg.	DK-252	DK-502	DK-582	DK-802	DK-812	Avg.
Electrical Properties													
Volume Resistivity at I kilovolt (ohm-cm)													
At RT: after 1 minute	1.0E16	1.5E16	1.2E16	1.5E16	1.5E16	1.8E16	1.5E16	1.3E16	1.5E16	2.1E16	1.7E16	1.9E16	1.7E16
after 3 minutes	2.8E16	3.8E16	3.3E16	3.6E16	3.9E16	5.0E16	3.9E16	4.2E16	4.2E16	5.7E16	4.6E16	5.0E16	4.7E16
At 200°F: after 1 minute	1.6E13	9.7E13	2.3E13	5.8E12	2.2E14	7.4E13	7.1E13	7.9E13	7.6E13	1.1E13	1.2E14	6.5E13	7.1E13
after 3 minutes	1.7E13	1.2E14	2.6E13	5.9E12	2.3E14	9.2E13	6.3E13	9.0E13	8.4E13	1.1E13	1.4E14	7.7E13	6.3E13
Dielectric Constant (10^6 Hz)	2.5	2.5	2.5	2.5	2.6	2.5	2.5	2.6	2.5	2.5	2.6	2.6	2.6
Dissipation Factor (1 k Hz)	0.010	0.021	0.020	0.017	0.020	0.020	0.020	0.015	0.014	0.013	0.015	0.016	0.015
Dielectric Strength	781	935	905	885	781	901	885	750	--	749	716	--	--
Thermal Properties													
Tg (°C, TMA)	-77/80	-80	-75	-78	-80	-78	-78	-77	-78	-80	-84	-81	-80
Mechanical Properties													
Hardness, Shore A (1/10 sec)	92/89	70/65	76/71	78/75	73/68	73/68	74/69	82/76	88/84	83/80	82/78	87/84	84/80
Ultimate Tensile Strength (psi)	1644	1065	1314	1080	987	1019	1093	1503	1837	1762	1748	1064	1583
Ultimate Tensile Elong. (%)	353	255	352	170	223	202	240	222	233	147	209	182	199
100% Modulus (psi)	971	464	572	751	499	562	570	965	1107	1281	1106	927	1077
Tear Strength, Die C (lbs./inch)	369	157	212	144	154	169	167	224	355	186	240	184	238

Table 8. Epoxy Encapsulants Tested for Electrical Performance (Batches sizes mixed, in grams, were 4-5 times the parts by weight shown in the table. All were cured 16 hours at 80°C.)

Formulation Ingredients	Formula 456	Formula 459	Standard 6/4 Epon/Versamid	"Reverse Ratio" Epon/Versamid
<u>Epoxy Resins</u>				
Shell Epon 826	50	75		
Ciba-Geigy (formerly Dow) XU-71790.04	25			
Shell Epon 828			60	37.6
<u>Curing Agents</u>				
Ancamine 2049	12.5	12.5		
Jeffamine D-230	12.5	12.5		
Versamid 140			40	62.4
Shin-Etsu KF-865 degassing aid	none	several drops	several drops	several drops

Figure 10. Volume Resistivity (1 KV/1 minute) for Urethane Elastomers and Epoxy Encapsulants.

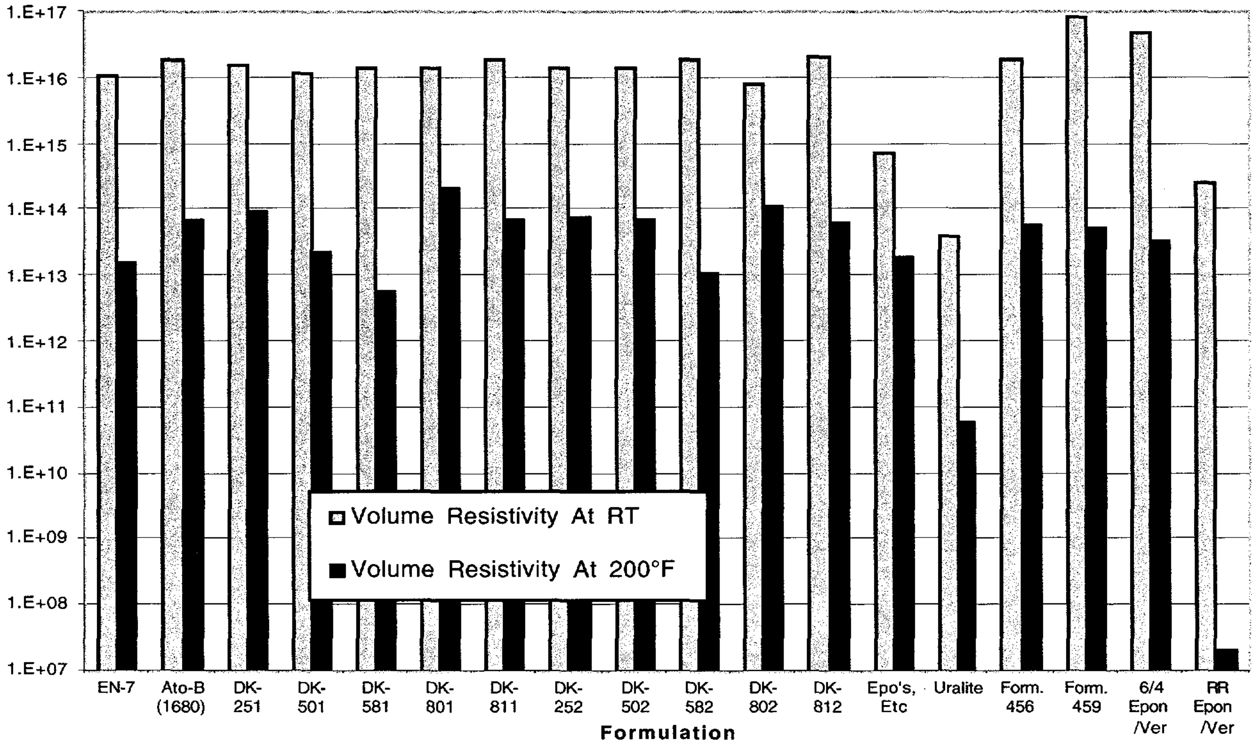
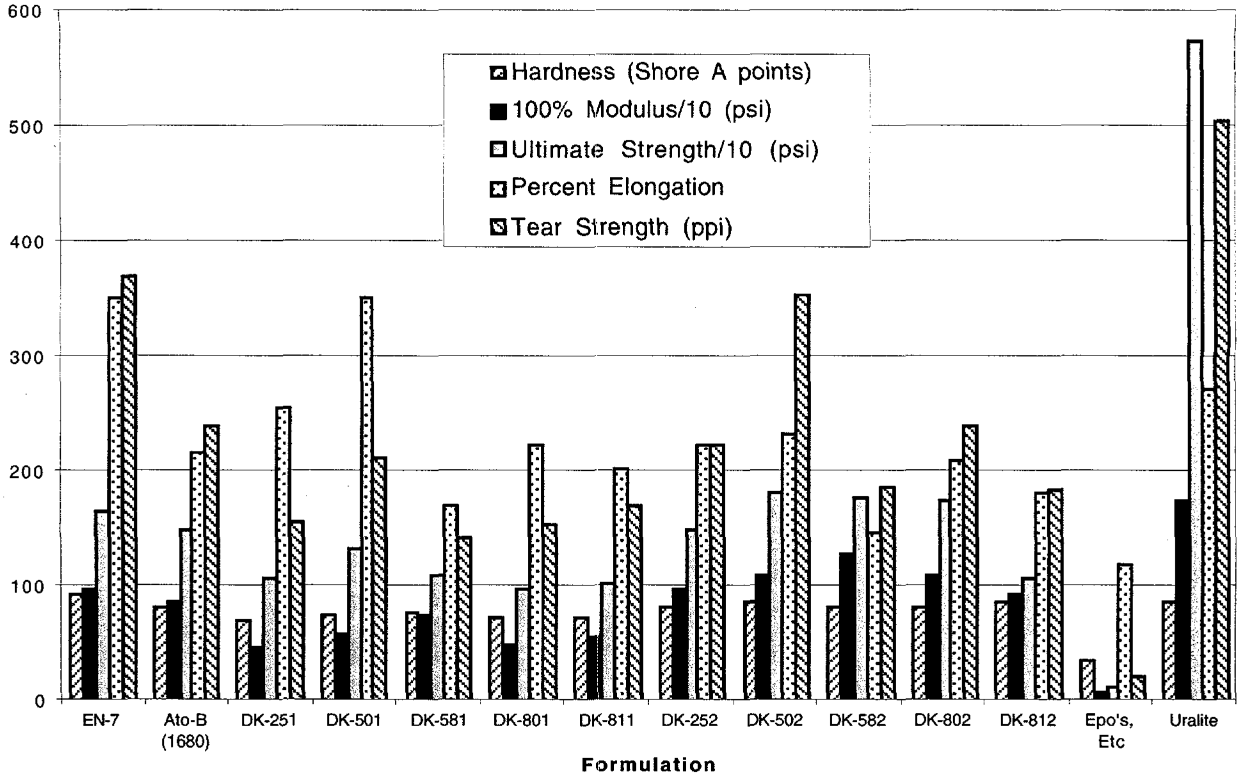


Figure 11. Mechanical Properties for Formulated and Commercial Urethane Elastomers.

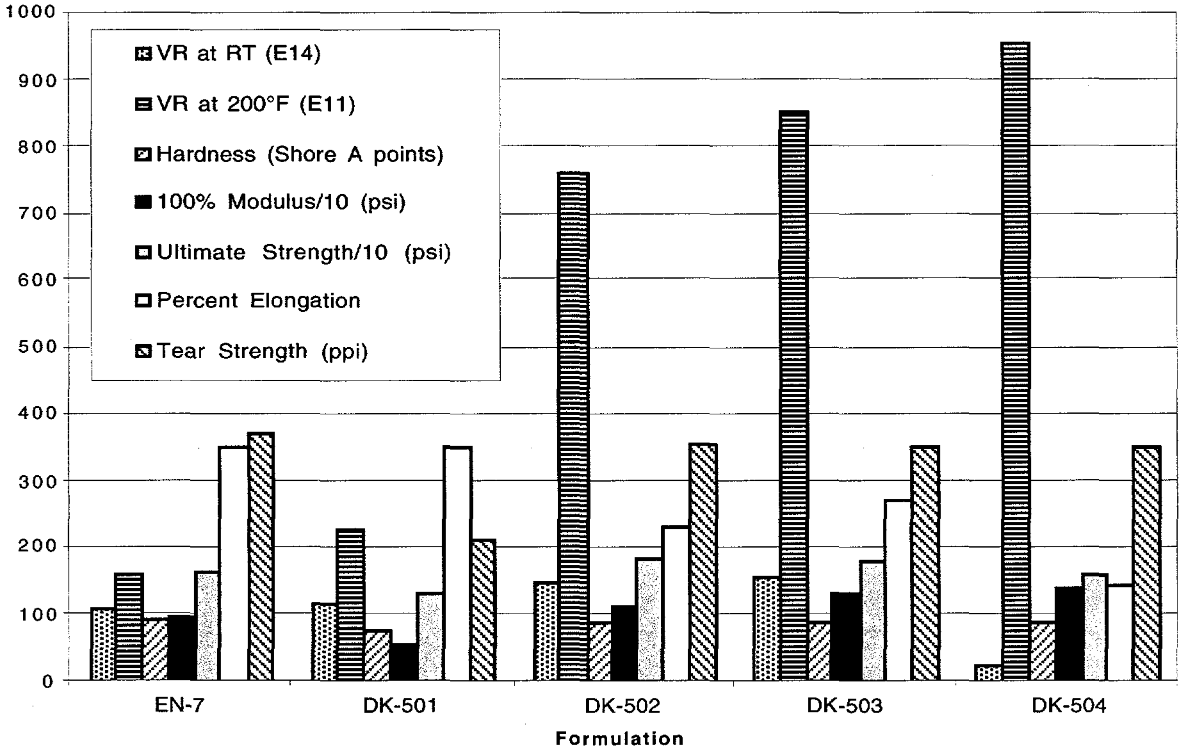


Two additional formulations based on Isonate 50 (DK-503 and DK-504) were evaluated to see what effect slightly higher levels of EN-7B would have on mechanical and overall performance. These compositions and weight percents were shown earlier in Table 6. The weight percent of EN-7B in DK-504 was very close to that in EN-7 itself (15.9 vs 15.8). As shown in Table 9 and Figure 12, there was no increase in either tear strength or hardness beyond the performance of DK-502 and all the formulations had similar Tg values. DK-502 and 503 generally had similar mechanical performance profiles while DK-504 showed a deterioration of elongation. There was no major or consistent change in volume resistivity, a potential consequence of the reduced butadiene content, and it was actually improved slightly at 200°F (93.3°C). The lower level of catalyst and chain extender in DK-502, compared to DK-503, would be expected improve potlife and processability and it therefore remained the preferred formulation.

Table 9. Electrical, Thermal and Mechanical Performance of DK-50X Series

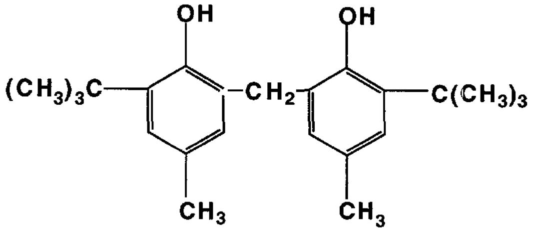
Material	EN-7	DK-501	DK-502	DK-503	DK-504
Electrical Properties					
Volume Resistivity at I kilovolt (ohm-cm)					
At RT: after 1 minute	1.0E16	1.2E16	1.5E16	1.6E16	2.4E15
after 3 minutes	2.8E16	3.3E16	4.2E16	4.3E16	4.7E15
At 200°F: after 1 minute	1.6E13	2.3E13	7.6E13	8.5E13	9.5E13
after 3 minutes	1.7E13	2.6E13	8.4E13	1.0E14	1.1E14
Dielectric Constant (10^6 Hz)	2.5	2.5	2.5	2.6	2.6
Dissipation Factor (1 k Hz)	0.010	0.020	0.014	0.013	0.012
Dielectric Strength	781	905	--	--	--
Thermal Properties					
Tg (°C, TMA)	-77/80	-75	-78	-80	-80
Mechanical Properties					
Hardness, Shore A (1/10 sec)	92/89	76/71	88/84	88/84	88/84
Ultimate Tensile Strength (psi)	1644	1314	1824	1797	1596
Ultimate Tensile Elong. (%)	353	352	233	272	144
100% Modulus (psi)	971		1107	1307	1389
Tear Strength, Die C (lbs/inch)	369	212	355	353	352

Figure 12. Electrical and Mechanical Properties of DK-50X Elastomer Series.



Antioxidant

EN-7 contains an antioxidant, Cyanox 2246 from Cytec Industries, which is also recommended in the Polybd formulations suggested by Elf Atochem. The antioxidant minimizes oxidative crosslinking and degradation of the residual double bonds in the polybutadiene backbone. Typically a fixed level of 0.1 gram was added to Atochem formulations having total weights of from about 120 to 200 grams. Conap adds 0.1 weight percent to EN-7 Part A which would provide 0.1 gram in 119 grams of total resin.



Cyanox 2246:

2,2'-(methylene-bis(4-methyl-6-t-butyl phenol)

The second series (XX2) of formulations were repeated and included 0.1 gram of antioxidant per total weights of 120-135 in the repeated series. The antioxidant was predissolved in the Polybd/EN-7B premix, using heat and stirring, although it could also be dissolved in the isocyanate.

No significant effect of the antioxidant on electrical or mechanical performance was expected or noted. Detailed test results are contained in Appendix E. In the preceding tables and figures of the test results, both the original and the antioxidant modified versions of the XX2 series were averaged to provide a single value for each formulation.

Thermal Expansion

Coefficients of thermal expansion were measured for EN-7 and for formulation DK-502. Similar CTE values were found for both over a temperature range of -40 to 110°C.

Multiple samples, each a small disk cut from a larger casting with a height of about 3 mm, were tested for each material. Each test included multiple heating and cooling cycles which showed good reproducibility when the first step included a one minute hold at elevated temperature. Earlier runs without this initial step often showed highly variable results even within a single sample. Such preliminary hold procedures were used in a previous Sandia study of CTE values for a range of polymeric materials used in weapon production[28]. All the tests were carried out on a Perkin-Elmer TMA7 using the following procedure:

1) Hold at 120°C for 1 minute
2) Cool from 120°C to -50°C at 5°C/minute
3) Heat from -50°C to 120°C at 5°C/minute
4) Repeat steps 2 and 3 two more times.

CTE values were determined over three temperature ranges: -40 to -10°C, -10 to 40°C, and 40 to 110°C. The midrange data often showed a very light break in the slope at about room temperature while the upper and lower ranges appeared linear. Average CTE values in ppm/°C (ppm = parts per million) for all the samples tested are shown below. The CTE value found for EN-7 in the survey referenced above was 171 ppm/°C between -50 and 20°C.

Resin	-40 to -10°C	-10 to 40°C	40 to 110°C
EN-7	172	206	240
DK-502	173	191	218

The similarity in CTE performance suggests that no differences should be expected in thermal cycling stresses for encapsulated components. If anything, the new formulation showed slightly lower CTE values and might result in reduced stresses.

Adhesive Testing

Lap shear adhesive testing (ASTM D1002) on aluminum was carried out on the XX2 formulation series as well as DK-503 and 504 to compare the new formulations to EN-7. Published work[29] by Elf Atochem indicates that a formulation similar to those evaluated here showed excellent adhesion to aluminum or steel, even to oily surfaces or after exposure to boiling water or freezing. The tests here were carried out on belt sanded coupons with no primers or other surface treatment. The bond thickness was not controlled.

The results are shown in Table 10 and show a range of performance. All the samples showed adhesive rather than cohesive failure. DK-502, the preferred replacement formulation, showed adhesive strength comparable to EN-7, and DK-503 also showed good adhesive performance. The remaining formulations showed lower adhesive strengths in this series of screening tests. No cause for these performance differences was apparent. Future adhesive testing would be appropriate for specific applications if critical.

Table 10. Lap Shear Adhesive Strength Values of Urethane Elastomers

Formulation	Adhesive Shear Stress (psi)
EN-7	1161
DK-252	490
DK-502	1361
DK-582	491
DK-802	471
DK-812	400
DK-503	971
DK-504	721

Cable Insulation Testing

Application tests, identical to those carried out earlier with the Y-12 prepolymer materials, were carried out at Kansas City on the first set of replacement formulations using SA2404-11 connectors. Results for both the Y-12 and Sandia materials are shown in Figures 13 and 14. The tests indicate similar performance for all five of the Sandia formulations as well as the EN-7 control. The results for the Y-12 materials gave slightly higher test values but were also comparable to the EN-7 control tested with that group. The limited number of available connectors allowed only one sample to be encapsulated with each of the Sandia formulations rather than the three samples encapsulated with each Y-12 formulation. All the Sandia samples and the EN-7 control were encapsulated at Sandia and tested at Kansas City as a group. Similar tests were not carried out on the second Sandia formulation series although the other dielectric tests carried out suggest that no difference in performance would be expected.

The SA2404-11 connector contains 19 pins. Each connector was tested between six different pin selections (2-10, 2-all, 19-all, 1-all, 18-all 10-all) at a DC voltage of 750 volts and that data was then averaged to give an overall connector insulation value. Tests were carried out at 75, 165 and 200°F (23.9, 73.9 and 93.3°C). The unencapsulated connectors were tested in 1998 as were the four test cables and those results are shown in Figures 15 and 16. Connector and cable differences might clearly contribute to slight variances in the test data beyond differences due to the encapsulant material. Only one cable, number 4, showed performance significantly different from the other cables, however, and that cable was not used for any of the Sandia/CA tests. Table 11 lists the connectors and cables used to test each encapsulant.

A critical parameter, affecting connections within the test equipment, is the relative humidity which is preferably kept below 40% for such tests. Humidity was difficult to control during the tests on the Sandia samples due to building modifications at Kansas City since the Y-12 samples were tested and this may account for the slightly lower resistance values measured. Two tests series carried out with the Sandia samples at relative humidities above 50% gave anomalous and unreliable results. A final test series in June 99 at 48% RH gave results with no abnormal behavior and is reported here.

Table 11. Connector and Cable Parameters for Encapsulant Resistance Tests

Encapsulant	Connector Number	Connector Resistance Before Encapsulation (75-200°F)	Cable Number	Test Cable Resistance (70-165-200°F)
DK-251	25	2.79E13-6.40E11	1	2.83E13-7.25E12-2.84E12
DK-501	28	2.15E13-4.57E11	1	"
DK-581	29	2.00E13-4.90E11	2	1.31E13-1.56E13-7.04E12
DK-801	26	1.53E13-9.04E11	2	"
DK-811	27	1.52E13-3.34E11	3	3.06E13-1.73E13-7.04E12
EN-7	30	1.42E13-3.07E11	3	"

Figure 13. Insulation Resistance of Y-12 Prepolymer Encapsulant Materials and EN-7 Control.

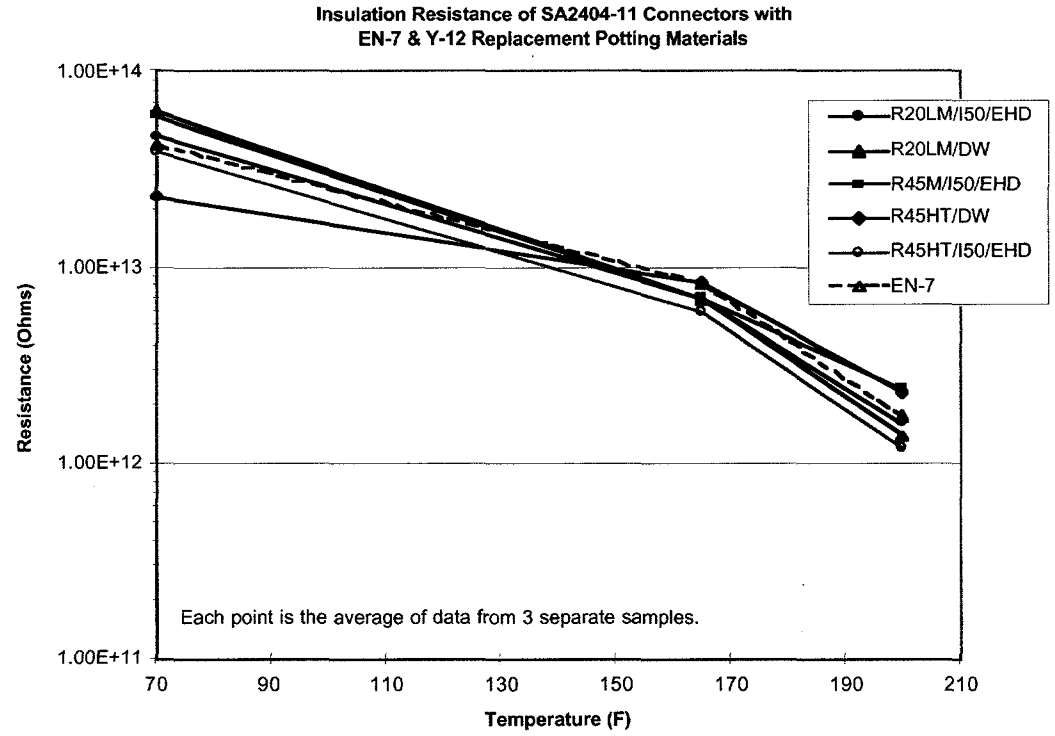


Figure 14. Insulation Resistance of Sandia Formulated Encapsulant Materials and EN-7 Control.

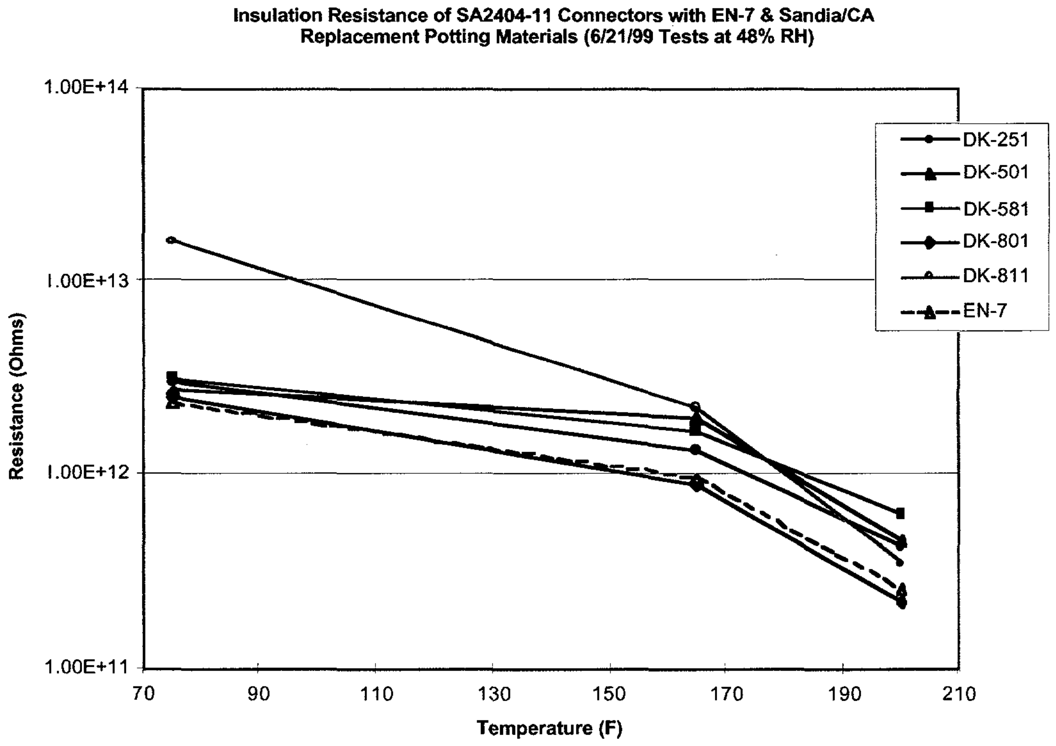


Figure 15. Connector Resistance Before Encapsulation.

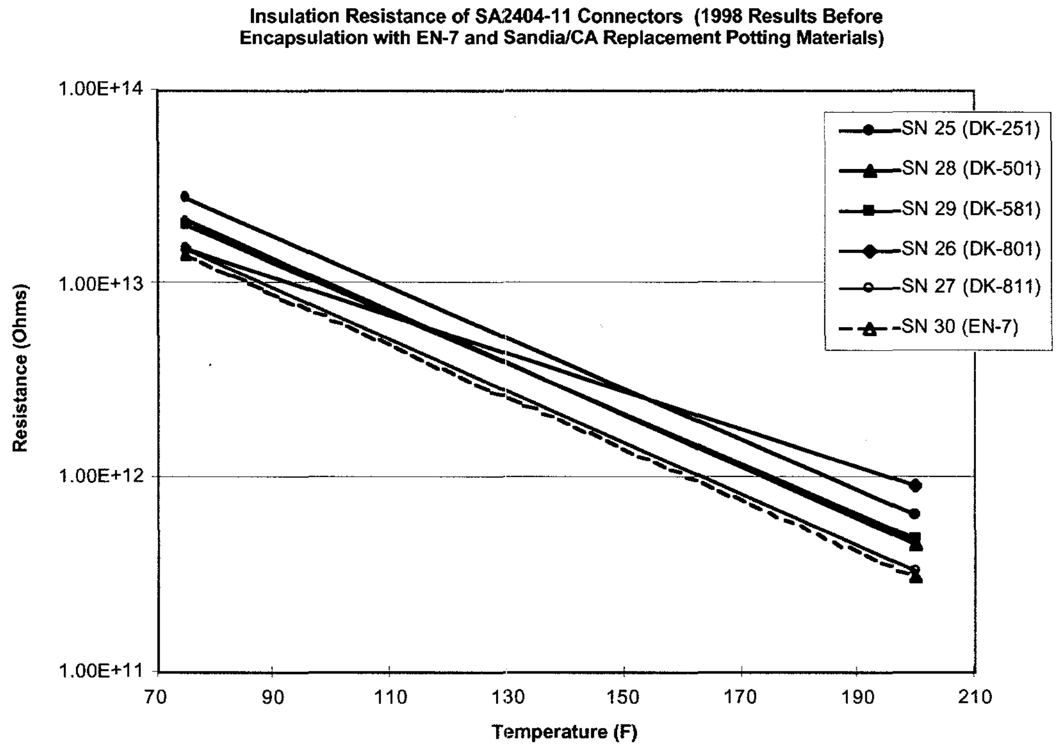
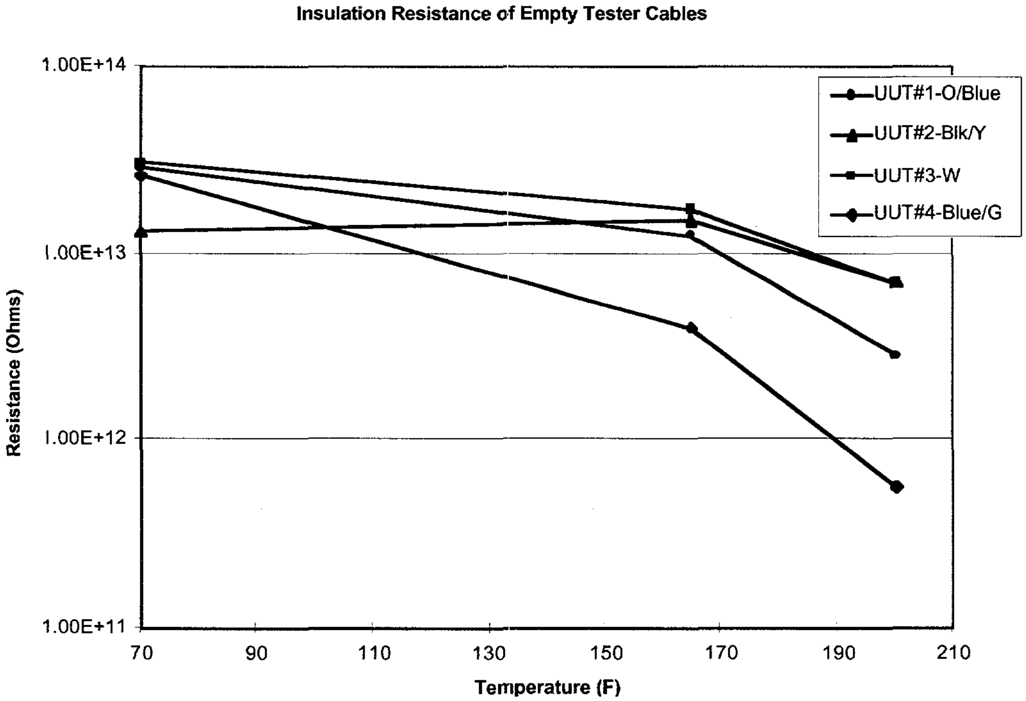


Figure 16. Cable Resistance Tests.

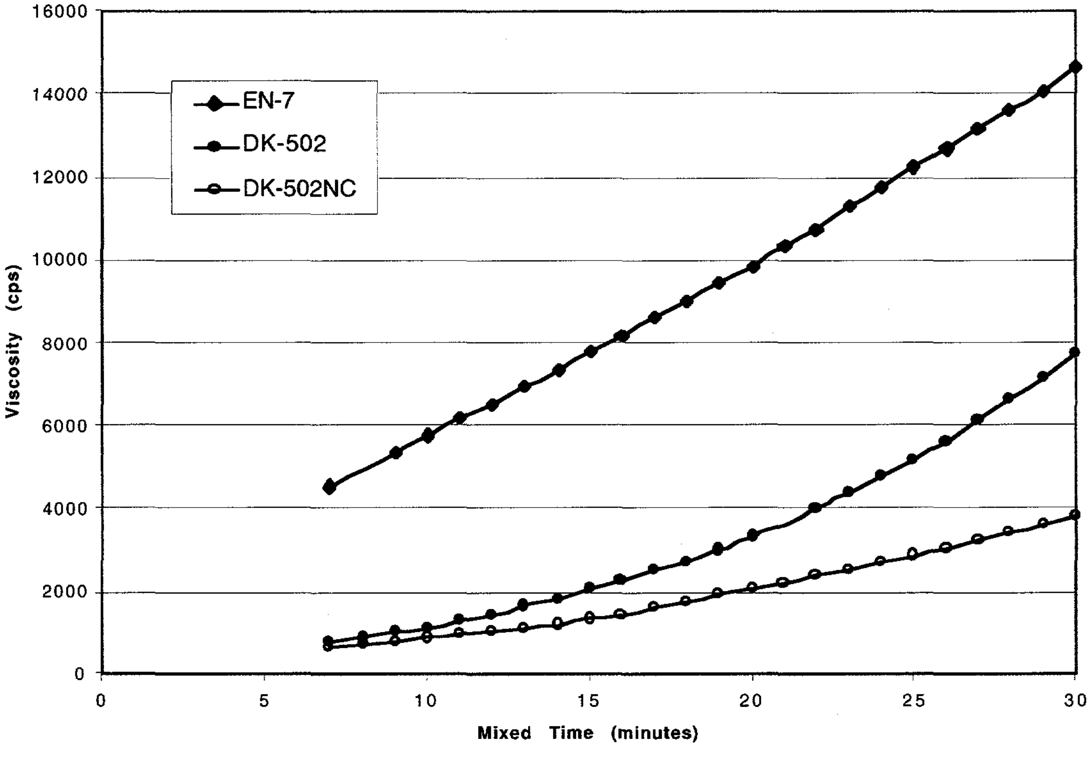


Potlife Comparisons and DK-502NC Evaluation

Figure 17 shows the viscosities of EN-7 and DK-502 at 30°C in a cone and plate viscometer (number 41 spindle). Each plot is the average of two viscosity runs. The time up to 7 minutes was consumed by resin mixing, resin degassing and addition of a resin sample to the viscometer. The circulating temperature control and heat mass of the viscometer cup would be expected to mitigate any exotherm effects during these measurements. Under these controlled conditions, the lower viscosity of DK-502 is apparent. While the viscosity of the EN-7 rose in a linear fashion up to 30 minutes, the DK-502 showed an increasing rate of viscosity rise, perhaps due to the different chain lengths of the Polybd and EN-7B diol reactants.

When the temperature of the mixed resins left in a cup was monitored, however, the EN-7 batch (119 grams total) rose only to about 45°C while the DK-502 batch (120 grams total) rose to about 63°C and was hot to the touch. The processing potlife, when judged by the "pourability" of the cup materials, was roughly 40 minutes for the EN-7 and 25 minutes for the more exothermic DK-502. While the initial viscosity of DK-502 is, therefore, significantly lower than that of EN-7, the higher curing exotherm clearly reduces the potlife if the resin temperature is not controlled. That higher exotherm probably results from the absence of a prepolymerization step in DK-502. Since many encapsulation processes do not provide for continuous temperature control of the materials and may also use a range of batch sizes, it would be desirable to have a longer potlife under those conditions.

Figure 17. Formulation Viscosity at 30°C (Controlled exotherm).



In order to improve the processability of DK-502, the same formulation was evaluated in the absence of the ferric acac catalyst present in the EN-7B portion. The two diols (2-ethyl-1,3-hexane diol and N,N'-(2-hydroxypropyl)aniline) used in EN-7B were preblended using a 1/1 weight ratio with no added catalyst and substituted in the formulation, now designated DK-502NC (NC = no catalyst). It should be noted that the two diols must be thoroughly blended to avoid phase separation. A roller was used in this case and no phase separation or crystallization of the Voranol 220-530 was noted after the diols had been thoroughly mixed. Use of this simple diol blend in place of EN-7B also eliminates problems associated with crystallization of the ferric acac catalyst during storage and the need to carefully reconstitute this component. It was also noted that preblending of this diol mixture with the Polybd was important to avoid inhomogeneous reactions of the isocyanate portion with non-uniform mixtures of the Polybd and the chain extenders. This seemed to be less critical, surprisingly, in the catalyzed formulations.

The potlife at 30°C was clearly improved with DK-502NC as shown in Figure 17. The potlife of the cup material (about 120 grams) was also significantly extended, even beyond that observed for EN-7. The observed exotherm reached about 50°C, similar to EN-7 and about 15°C lower than seen with the catalyzed formulation, and the mixture remained pourable for almost one hour. The size of such exotherms, and the potlife, will clearly be dependent on batch size, filler level if any, and the heat dissipation of the container used. The effects of fillers in these elastomer formulations have not been investigated, but would be expected to decrease the processability of EN-7, which is already highly viscous, and perhaps increase the processability of DK-502 and DK-502NC by reducing the exotherm. The specific behavior of any filled formulation would depend on the type and level of filler used as well as the batch size mixed.

Castings of DK-502NC were also prepared to evaluate the mechanical performance of the uncatalyzed formulation. The cure schedule remained at 16 hours at 80°C. These properties are shown in Table 12 along with comparisons to DK-502 and EN-7. More detailed data in contained in Appendix E.

Table 12. Electrical and Mechanical Performance of EN-7, DK-502 and DK-502NC

Property	EN-7 (ferric acac catalyzed)	DK-502 (ferric acac catalyzed)	DK-502NC (no catalyst)
Vol. Resist. at Room Temp. (ohm-cm at 1/3 min.)	1.10E16 / 2.90E16	1.47E16 / 4.02E16	1.27E16 / 3.30E16
Volume Resistivity at 200°F (ohm-cm at 1/3 min.)	1.60E13 1.68E13	7.59E13 / 8.39E13	3.48E13 / 3.73E13
Dielectric Constant at RT (1/10/100/1000 kHz)	2.77/2.73/2.71/2.49	2.87/2.82/2.77/2.54	2.96/2.90/2.84/2.59
Dielectric Constant at 200°F (1/10/100/1000 kHz)	3.74/3.39/3.07/2.64	3.49/3.26/3.06/2.69	3.58/3.35/3.14/2.73
Shore A Hardness (1/10 sec.)	92 / 89	88 / 84	84 / --
Tensile Stress at 100% Elong.	971 psi	1107 psi	997 psi
Ultimate Tensile Strength	1644 psi	1824 psi	1704 psi
Ultimate Tensile Elongation	353%	233%	337%
Tear Strength	369 ppi	355 ppi	335 ppi

All three materials gave similar dielectric performance. The mechanical properties show DK-502NC to be slightly softer and higher in tensile elongation than DK-502, reflecting the difference in catalyst content. The properties of DK-502NC were very similar to those of EN-7 except in Shore A Hardness. It is unclear if the slightly softer nature of DK-502NC would be advantageous or disadvantageous and might depend on the specific application. Higher cure temperatures or longer cure schedules would also change the mechanical properties of DK-502NC to some extent and have not been investigated.

DK-502NC Formulation Processing

For reference, the material specifications at Kansas City Plant are 2519603 for EN-7 and 2519605 for EN-8. Both were heavily revised in 1997, primarily to clarify the procedures for reconstituting the ingredients prior to use if they have become inhomogeneous due to crystallization of the ferric acac catalyst. In addition to the material specification, process specifications 9927087 (EN-7) and 9927089 (EN-8) describe their use for the encapsulation of connectors or other hardware. These include a wide variety of processing and curing conditions.

The recommended processing requirements for Formula 502NC would involve the preliminary preparation of a well mixed pre-blend of the Polybd, the ethylhexane diol, the Voranol 220-530, the Cyanox 2246 antioxidant and the KF-865 degassing aid into a single component. Such preblends appear stable at ambient conditions with no phase separation. Use of such a pre-blend reduces the formulation processing to a 2-component operation in which the pre-blend and the Isonate 50 are mixed at a 73.3/26.7 ratio (as shown in Table 13 below) plus any required fillers, degassed and dispensed as appropriate for the application. The batch size should be the minimum required in order to reduce the reaction exotherm during degassing and processing. Degassing is facilitated by the presence of trace amounts of KF-865 amino-functionalized silicone. The level added is not critical and should be in the range of 100 ppm (about .04-.05 grams or 3-4 drops per 500 gram batch). This is most easily measured during the preparation of a large pre-blend batch of 500 grams or even larger.

Table 13. DK-502NC Formulation (100 parts total)

Parts	DK-502NC Polyol Preblend Portion	parts	DK-502NC Isocyanate Portion
59.90	R45HTLO Polybd polybudiene polyol (Elf Atochem, formerly Arco)	26.7	Isonate 50 (Dow Chemical)
6.65	1,3-dihydroxy-2-ethylhexane (Aldrich)		
6.65	N,N'-(2-hydroxypropyl)aniline (Voranol 220-530 from Dow)		
0.09	Cyanox 2246 Antioxidant (Cytec Industries)		
0.01	KF-865 silicone fluid (Shin-Etsu)		
73.3	TOTAL	26.7	TOTAL

Summary

A range of mix-and-pour polyurethane elastomer formulations have been evaluated as TDI-free replacement materials for EN-7, a widely used encapsulant in weapon applications. A general review of the history of such materials within the DOE complex has also been provided which notes the previous difficulty in matching the dielectric performance of EN-7.

All the formulations used polybutadiene polyols and crosslinking diols similar to those used in EN-7. The TDI was replaced by various commercially available liquid diisocyanates. All the formulations gave dielectric properties at room temperature and at 200°F (93.3°C) comparable to EN-7, a key requirement for some applications. Mechanical properties (hardness, tensile strength, tensile modulus, tensile elongation, and tear strength) varied with the different diisocyanates although several of the formulations provided acceptable property profiles. The mechanical performance of the formulations based on Isonate 50 was most similar to EN-7 and those formulations were evaluated in the greatest depth.

Because there is no prepolymerization of any of the ingredients, the reaction exotherm of these formulations were higher than observed with EN-7 and resulted in a shorter potlife if the material temperature was uncontrolled. This was mitigated by removing the ferric acac catalyst from the preferred formulation and resulted in a potlife in the preferred formulation similar to EN-7 but with a significantly lower starting viscosity. Removal of the catalyst also eliminates some the processing problems associated with precipitates formed during storage.

Based on the above evaluations, the uncatalyzed formulation designated DK-502NC is recommended as a general replacement for EN-7. Simple two-component processing is possible after the preparation of a stable preblend of the polyols, antioxidant and degassing aid used. This is then mixed with the liquid Isonate 50 component and any needed fillers, degassed, poured and cured in procedures similar to those used for EN-7.

References

1. T.M. Schnorr et al , "Mortality of Workers Exposed to Toluene Diisocyanate in the Polyurethane Foam Industry," Occupational and Environmental Medicine, 53, 703-707 (1996)

2. D.L. Stoltz and E.W. Grotheer, KCD, memo to John Sayre, SNL, "Development of Alternatives to TDI Containing Materials," dated December 3, 1991.

3. C. Arnold, "Replacement Materials for Adiprene L-100/MOCA - A Survey Report," SAND74-0064 (1975)

4. C. Arnold, SLA-73-1013 (1973)

5. H.W. Lichte, H.D. Johnson and J.L Montague, "Evaluation of Hexcel Uralite 3121S Adhesive for Assembly Processes," Pantex Plant, No. 201 (1975)

6. R.R. Lagasse, "Development of a Structure-Property Correlation for Castable Urethane Elastomers," SAND77-0822 (1978)

7. A.J. Quant, D.D. Drumond and R.R. Lagasse, "Apocure 601 - A MOCA Replacement," SAND79-0630 (1979)

8. F.G. Childress, "Urethane Adhesives - L100/MOCA Substitutes," Oak Ridge Y-12 Plant Report, Y-DA-5771 (1974)

9. F.G. Childress, C.E. Miller, and A.K. Zava "Urethane Adhesives - L100/MOCA Substitutes," Oak Ridge Y-12 Plant Report, Y-1952 (1974)

10. George Hammond, "Properties of Adiprene L-100/MOCA as a Room-Temperature-Cured Adhesive and Possible Substitutes for It," LLNL, UCID-16329 (1973)

11. H.G. Hammond et al, "Two Urethane Elastomers as Substitutes for Adiprene L-100 Cured with MOCA," LLNL, UCRL-75591 (1974)

12. H. George Hammond, "Properties of Three Adiprene-Based Systems," LLNL, UCRL-52044 (1976)

13. D.J. Caruthers et al, "Hydrolytic Stability of Adiprene L-100 and Alternate Materials," Bendix/Kansas City Division report, BDX-613-1489 (1976)

14. H.G. Hammon, L.P. Althouse and D.M. Hoffman, "Development of Halthane Adhesives for Phase 3 Weapons: Summary Report." LLNL, UCRL-52943 (1980)

15. D.J. Caruthers, "Adhesion of Adiprene L-100/Cyanacure to Cable Materials," KCP, BDX-613-3086 (1984)
16. R.L. Myers and E.V. Thomas, "Characterization of Polyurethane Systems Which Contain Low Levels of Free TDI," SAND94-2031 (1995)

17. T.R. Guess, "Isothermal Aging of Three Polyurethane Elastomers," SAND96-1028 (1996)

18. M.H. Wilson, "Cyanacure Replacement Study," KCP-613-4948 (1992)

19. Greg Manke and Mark Wilson (AlliedSignal/FM&T), unpublished data

20. "Polybd Resins in Electrical Applications," Elf Atochem (1990) plus insert on catalyst comparisons. This brochure cites as a reference G.M. LeFave, "A New Class of RTV Insulation Materials. Functionalized Polybutadiene Based Liquid Polymers," 10th Elec. Insul. Conf. Proc., Chicago, IL, Sept. 20-23 (1971)

21. K.C. Frisch, H.B. Yokelson et al, "Polyurethane Elastomers Based Upon Novel Hydrocarbon-Based Diols," Cellular Polymers, Vol. 15, pp 395-416 (1996) (Amoco DIFOL materials)

22. Krasol brochure and product list from Drobny Polymer Associates, 11 Quail's Way, Merrimack, NH 03054.

23. M.A. Masse and L. Handlin, Jr., US Patent 5,864,001, "Polyurethanes Made with Polydiene Diols, Diisocyanates, and Dimer Diol Chain Extender," assigned to Shell Oil Company (1999)

24. G. Oertel, "Polyurethane Handbook," 2nd edition, Hanser Publishers (1993)

25. Michael Szycher, "Szychers Handbook of Polyurethanes," CRC Press (1999)

26. Zygmunt Wirpsza, "Polyurethanes: Chemistry, Technology and Applications," Ellis Horwood, Ltd. (1993)

27. Epoxies, Etc. brochure dated 1995. www.epoxies.com

28. D.B. Adolf, SAND88-0777, "Coefficients of Thermal Expansion of Common Encapsulants," July 1988

29. R. Stretton and D.P. Braksmayer, "The Use of PolyBd Resin in Structural Adhesives," J. Adhes. Seal. Council, Spring 1998 Convention Proceedings

Appendix A: Potential Replacements for Adiprene L-100/Cyanacure

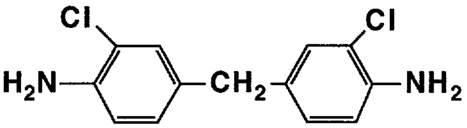
A May 1990 meeting (minutes published as a June 26, 1990 memo from Ramona Myers of Sandia/NM) of the "Alternate Polyurethane Systems Working Group" summarized the systems under consideration as replacements for Adiprene L-100/Cyanacure due to the discontinuation of Cyanacure production. All of the systems listed used aromatic amine crosslinkers similar to Cyanacure. Preliminary evaluations of the mechanical, thermal and processing characteristics of these candidates were carried out by the assigned personnel before the candidate list was narrowed down to Adiprene L-100/Ethacure 300 and the closely related system, Pet 90A/Ethacure 300. No inclusive compilation of the data gathered during those evaluations is available although preliminary results were published in an October 18, 1990 memo by Ramona Myers as minutes of the Oct. 10 meeting of the working group. Structures of the various diamine curing agents considered are shown in Figure A-1.

Work carried out by Ramon Myers of Sandia/NM was documented in a Sandia report (SAND94-2031, April, 1995). Work carried out by Mark Wilson of Kansas City was documented in an AlliedSignal report (KCP-613-4948, July 1992). Much of this work is also detailed in a series of memos through much of the 1990-1995 period authored by John Sayre of Sandia/NM containing the minutes of the DOE-complex working group evaluating alternative materials.

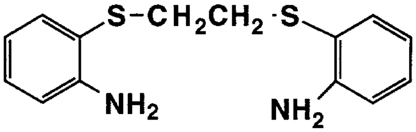
Polyurethane System	Participants Involved
TDI-based prepolymers:	
Adiprene L-100/Ethacure 300	Fred Larsen (KCP, now retired)
Adiprene L-100/Lonzacure	Fred Larsen (KCP, now retired)
Adiprene L-100/Baytec	Gerry Glasgow (Mound, now retired)
Adiprene L-100/MOCEA	George Dorsey (Y-12)
Adiprene L-100/Polacure	Mark Wilson (KCP) & Ramona Myers (SNL)
RN-1501/Ethacure 300	Mark Wilson (KCP) & Ramona Myers (SNL)
RN-1501/Lonzacure	Mark Wilson (KCP) & Ramona Myers (SNL)
RN-1501/Polacure	Mark Wilson (KCP) & Ramona Myers (SNL)
MDI-based prepolymers:	
Adiprene M-100 Series/Polacure	Mark Wilson (KCP) & Ramona Myers (SNL)
Adiprene M-100 Series/Polamine 1000	Renita Cook (LANL) & Ramona Myers (SNL)
Isonate 143L (now 2143L)/Polamine 1000	Renita Cook (LANL) & Ramona Myers (SNL)
PAPI Series/Polamine 1000	Renita Cook (LANL)
Halthane 88/Asilamine	George Dorsey (Y-12)
Halthane 88/XCE155	George Dorsey (Y-12)
Halthane 88/t-BTDA	Gerry Glasgow (Mound, now retired)

Figure A-1. Aromatic Amine Crosslinkers.

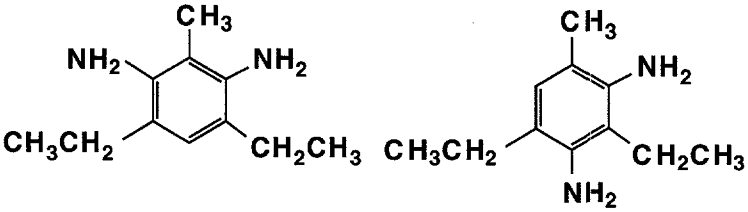
MOCA (m.p. 101°C)



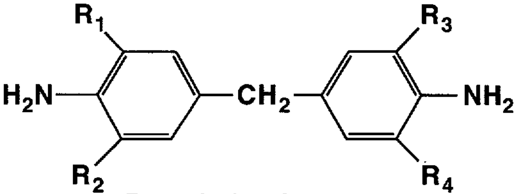
APOCure/Cyanacure/Versalink 138 (m.p. 75°C)



Ethacure 100 (liquid)

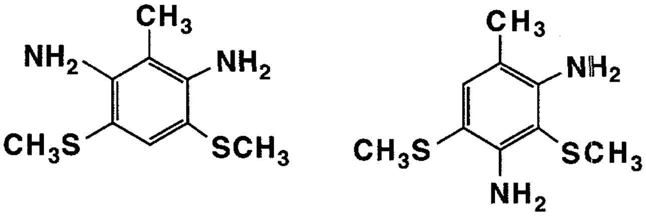


Asilamine 170 (liquid)

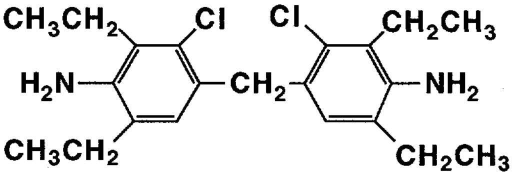


R = ethyl or isopropyl

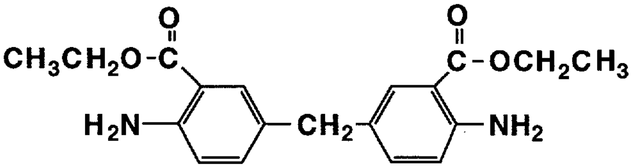
Ethacure 300 (liquid)



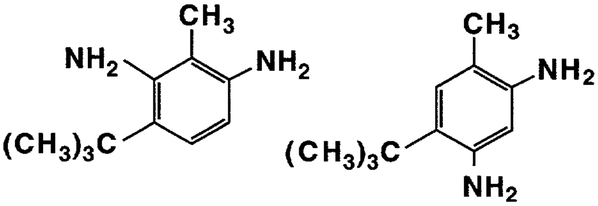
Lonzacure (m.p. 92°C)



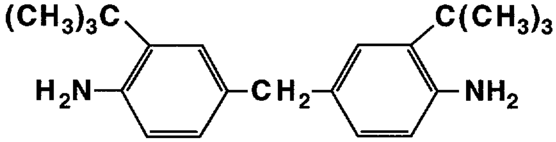
MOCEA (m.p. 106°C)



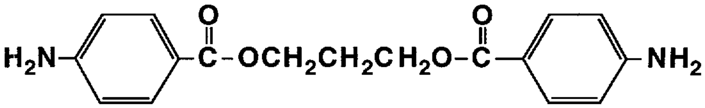
t-BTDA (m.p. 40°C)



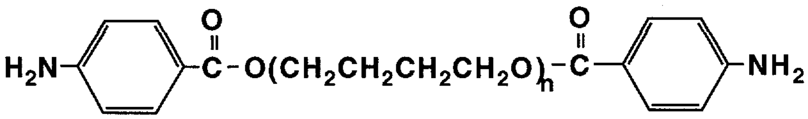
Air Products XCE 155 (m.p. 85°C)



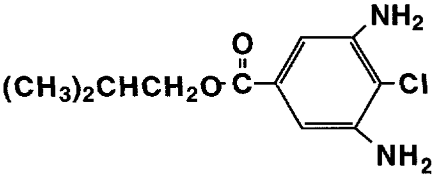
Polacure 740M (m.p. 126°C)



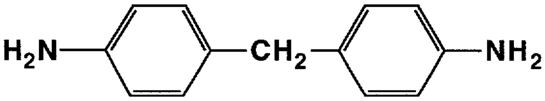
Polamine 1000 (liquid, m.p. 20°C)



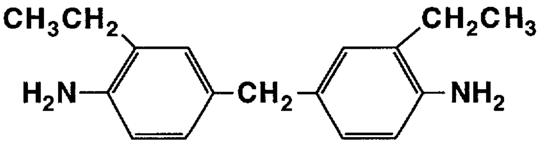
Baytec 1604 (m.p. 84°C)



MDA (m.p. 90°C, present in Shell Z & XU-205)



MBOEA (m.p. ?, present in XU-205)



(XU-205 = 10/40/40 MDA/MAOEA/MBOEA)

Appendix B: DOE Polyurethane Elastomer Encapsulants and Adhesives

An August 1992 meeting of the "Alternate Polyurethane Systems Working Group" summarized the various elastomer systems in use, used at one time, or evaluated in depth, and requested uniform data information on each material from assigned participants. While that ambitious compilation of data was not reached, the list of systems below had never previously been compiled. This list probably is not complete, particularly in regard to other commercial systems that may be in the stockpile. It should be noted that Adiprene L-100 has been used with four different curing agents and the simple and common designation of an elastomer as "Adiprene L-100" or, worse, "Adiprene", does not adequately identify the material.

Adiprene L-100/MOCA
Adiprene L-100/Cyanacure
Adiprene L-100/Ethacure 300
Adiprene L-100/BD/TMP

Adiprene L-315/BD/TMP

Adiprene M-467/Polamine 1000
Adiprene M467/Polamine 1000/PPG 2025

Adiprene L-42/Cyanacure/PPG 1025

Halthane 88 with assorted curing agents (Asilamine, t-BTDA, XC165)

EN-7, EN-8 and EN-9

Uralite 3121-S

Casmar 207

Urethane 7200

Aralhex

CPR 1009

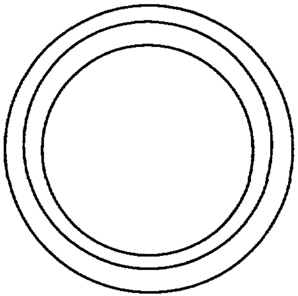
Pet90A/Ethacure 300

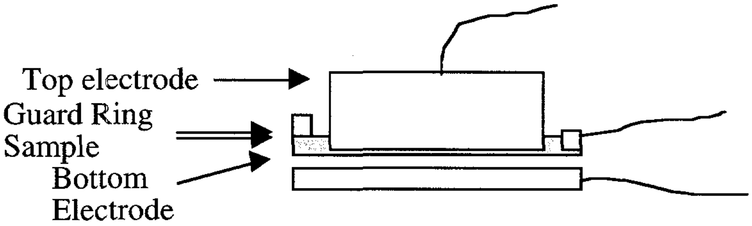
Appendix C: Dielectric Testing

Initial dielectric tests were carried out by Paul Beeson at Sandia, NM. This testing capability was later set up in Sandia, CA where most of the tests were run. Round-Robin comparisons between the two labs showed good agreement after some early trouble-shooting.

The early tests carried out by Paul Beeson in Sandia, NM used smaller brass electrodes with a 2 inch diameter top electrode, 4 inch bottom electrode and guard ring with an inner diameter of 2.3 inches. A larger set of electrodes with a 4.25 inch top electrode and 5 inch bottom electrode was designed by Paul Beeson and fabricated in the Sandia,NM machine shop for use in Sandia, CA. The guard ring had an inner diameter of 4.5 inches and the effective electrode area uses a diameter midway between the upper electrode and guard ring or 4.375 inches. The CA electrodes therefore had an effective surface area of 15.03 sq. in. (96.99 sq. cm.) and the area of the NM electrodes was 3.65 sq. in. (23.55 sq. cm.). The electrodes were enclosed in a oven for both faraday shielding and heating. Low noise test leads were used and all cable connections as well as the electrodes were carefully insulated.

The specific equipment used in California, all from Hewlett-Packard, consisted of a Model 4339B High Resistance Meter and a Model 4284A Precision LCR Meter along with low-noise leads (16117C).





All volume resistivity measurements except for some early tests and comparisons of resistivity vs. voltage in Sandia,NM were carried out at 1 kilovolt. Volume resistivities were measured both one minute, as called for in the ASTM procedures, and three minutes after the voltage was applied. The conductivity, as expected, dropped rapidly during the first minute and more slowly during the next two minutes.

Dielectric breakdown testing was carried out at AlliedSignal/FM&T in Kansas City.

Calculations:

Volume Resistivity = (Voltage x Electrode Area) / (Measured Current x Sample Thickness)

Dielectric Constant = (Measured Capacitance x Sample Thickness) / (Electrode Area x ε_0)

where ε_0 = electric field constant ($8.854 \times 10^{-12}\ \mathrm{Fm}^{-1}$)

Appendix D: Volume Resistivity vs. Time at Temperature

Anomalous resistivity results at 200°F (93.3°C) after one sample was heated for six hours instead of the standard two hours led to an investigation of the volume resistivity vs. time and temperature. A two hour heating period was used in the 200°F volume resistivity tests after preliminary trials with inserted thermocouples indicated that heating of the sample and electrodes for at least 1.5 hours was required to actually bring the sample to temperature. Both EN-7 and DK-581 were evaluated and both showed no significant change in resistivity on heat aging at 200°F for up to 20 hours. There was a clear correlation of resistivity to temperature observed during both the heating and cooling stages. These results are shown in Figures D-1 and D-2. The source of the particular discrepancy seen in the original sample was not determined, but the length of heating at temperature did not appear to be a significant parameter.

Figure D-1. Volume Resistivity (1 kV) of EN-7 vs. Time and Temperature

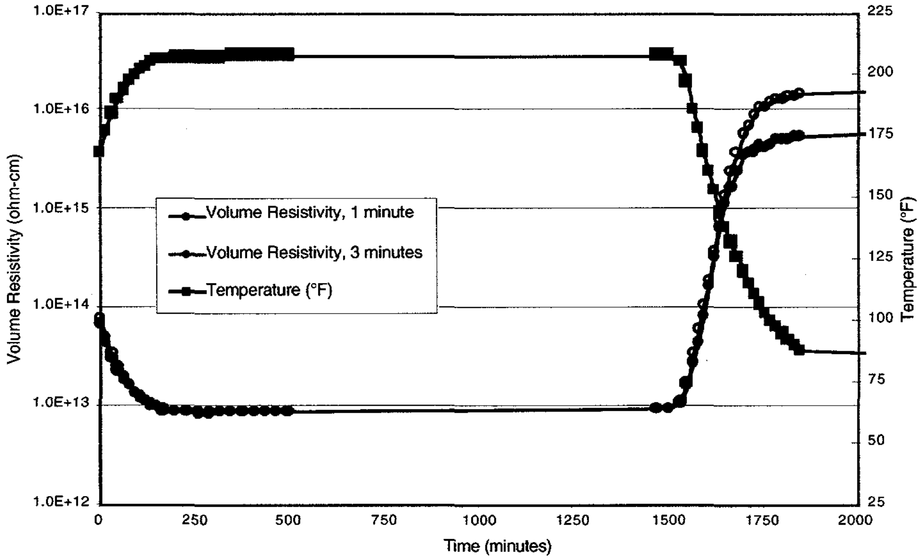
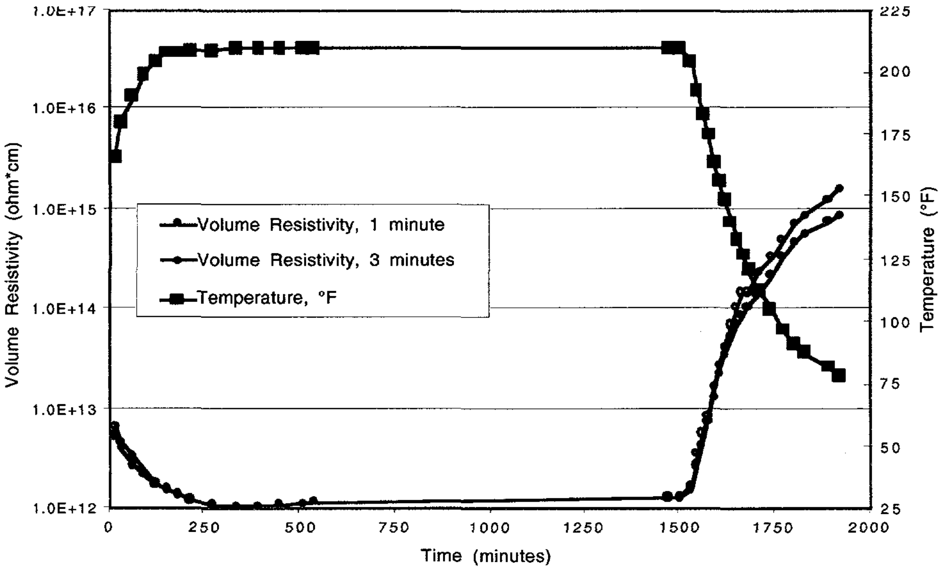


Figure D-2. Volume Resistivity (1 kV) of DK-581 vs. Time and Temperature



Appendix E: Test Data

Table E-1. Electrical Tests at Room Temperature

Sample Date	Formulation	I: 1 min.	I: 3 min.	Vol. Res.: 1 min.	Vol. Res.: 3 min.	1 kHZ Cp	K	D	10 kHZ Cp	K	D	100 kHZ Cp	K	D	1000 kHZ Cp	K	D	Sample Thick.
		Amps	Amps	ohm-cm	ohm-cm	Farads			Farads			Farads			Farads			cm
21898	EN-7	2.76E-11	1.03E-11	1.08E+16	2.89E+16	7.33E-11	2.78	0.0100				7.18E-11	2.72	0.0080				0.325
sample 2		2.92E-11	1.10E-11	1.01E+16	2.69E+16	7.33E-11	2.80	0.0099	7.24E-11	2.77	0.0083	7.17E-11	2.74	0.0083	6.63E-11	2.53	0.0550	0.328
43098		3.34E-11	1.22E-11	1.00E+16	2.74E+16	8.12E-11	2.73	0.0099	8.02E-11	2.70	0.0082	7.95E-11	2.68	0.0080	7.31E-11	2.46	0.0583	0.289
70899		2.32E-11	9.26E-12	1.31E+16	3.29E+16	7.44E-11	2.76	0.0081	7.37E-11	2.73	0.0071	7.31E-11	2.71	0.0072	6.71E-11	2.49	0.1528	0.318
	AVERAGE	2.84E-11	1.07E-11	1.10E+16	2.90E+16	7.56E-11	2.77	0.0095	7.54E-11	2.73	0.0079	7.40E-11	2.71	0.0079	6.88E-11	2.49	0.0887	
30498	AtoChem B w/ 2143L	1.87E-11	6.61E-12	1.56E+16	4.43E+16	7.66E-11	2.95	0.0170				7.32E-11	2.82	0.0160				0.331
sample 2		1.71E-11	6.01E-12	1.72E+16	4.89E+16	7.69E-11	2.96	0.0167	7.52E-11	2.89	0.0163	7.35E-11	2.83	0.0164	6.71E-11	2.58	0.0620	0.330
	AVERAGE	1.79E-11	6.31E-12	1.64E+16	4.66E+16	7.67E-11	2.96	0.0169				7.33E-11	2.82	0.0162				
31898	Atochem B w/ R1680	1.12E-11	6.53E-12	2.53E+16	4.33E+16	7.76E-11	3.10	0.0180				7.40E-11	2.96	0.0170				0.343
sample 2		2.14E-11	8.56E-12	1.38E+16	3.44E+16	7.74E-11	2.97	0.0176	7.56E-11	2.90	0.0171	7.38E-11	2.83	0.0173	6.73E-11	2.58	0.0630	0.329
	AVERAGE	1.63E-11	7.55E-12	1.95E+16	3.89E+16	7.75E-11	3.03	0.0178				7.39E-11	2.89	0.0172				
41698	DK-251	2.50E-11	9.60E-12	1.41E+16	3.67E+16	9.22E-11	2.95	0.0210				8.70E-11	2.79	0.0200				0.275
sample 2		2.24E-11	8.91E-12	1.57E+16	3.93E+16	9.16E-11	2.96	0.0214	8.89E-11	2.87	0.0205	8.65E-11	2.79	0.0200	7.78E-11	2.51	0.0711	0.277
	AVERAGE	2.37E-11	9.26E-12	1.49E+16	3.80E+16	9.19E-11	2.96	0.0212				8.68E-11	2.79	0.0200				
33198	DK-501	3.04E-11	1.02E-11	1.14E+16	3.38E+16	8.84E-11	2.89	0.0200				8.39E-11	2.75	0.0180				0.281
sample 2		2.91E-11	1.07E-11	1.18E+16	3.23E+16	8.83E-11	2.90	0.0200	8.58E-11	2.82	0.0190	8.38E-11	2.75	0.0180	7.57E-11	2.49	0.0677	0.282
	AVERAGE	2.97E-11	1.04E-11	1.16E+16	3.31E+16	8.83E-11	2.90	0.0200				8.38E-11	2.75	0.0180				
41498	DK-581	2.47E-11	1.08E-11	1.35E+16	3.10E+16	8.64E-11	2.92	0.0177				8.27E-11	2.79	0.0160				0.290
sample 2		2.20E-11	8.33E-12	1.54E+16	4.07E+16	8.67E-11	2.89	0.0165	8.47E-11	2.82	0.0160	8.29E-11	2.76	0.0162	7.51E-11	2.50	0.0671	0.286
	AVERAGE	2.33E-11	9.56E-12	1.45E+16	3.59E+16	8.66E-11	2.90	0.0171				8.28E-11	2.78	0.0161				
32398	DK-801	2.07E-11	7.95E-12	1.42E+16	3.70E+16	7.88E-11	3.03	0.0200				7.46E-11	2.87	0.0190				0.330
sample 2		1.93E-11	7.29E-12	1.53E+16	4.06E+16	7.87E-11	3.01	0.0200	7.65E-11	2.92	0.0195	7.45E-11	2.85	0.0196	6.76E-11	2.58	0.0653	0.328
	AVERAGE	2.00E-11	7.62E-12	1.47E+16	3.88E+16	7.87E-11	3.02	0.0200				7.45E-11	2.86	0.0193				
40298	DK-811	1.95E-11	7.30E-12	1.73E+16	4.61E+16	9.02E-11	3.02	0.0200				8.53E-11	2.86	0.0200				0.288
sample 2		1.72E-11	6.28E-12	1.95E+16	5.34E+16	8.86E-11	2.98	0.0202	8.61E-11	2.90	0.0198	8.38E-11	2.82	0.0203	7.54E-11	2.54	0.0704	0.289
	AVERAGE	1.83E-11	6.79E-12	1.84E+16	4.98E+16	8.94E-11	3.00	0.0201				8.45E-11	2.84	0.0202				
	XX1 SERIES AVG	2.30E-11	8.73E-12	1.48E+16	3.91E+16	8.70E-11	2.96	0.0197	8.44E-11	2.87	0.0190	8.25E-11	2.80	0.0187	7.43E-11	2.52	0.0683	

NOTE: Sample 2 indicates that a second test plaque was cut from the casting in the row above.

Table E-1. Electrical Tests at Room Temperature (continued)

Sample Date	Formulation	I: 1 min.	I: 3 min.	Vol. Res.: 1 min.	Vol. Res.: 3 min.	1 kHZ Cp	K	D	10 kHZ Cp	K	D	100 kHZ Cp	K	D	1000 kHZ Cp	K	D	Sample Thick.	den.
		Amps	Amps	ohm-cm	ohm-cm	Farads			Farads			Farads			Farads			cm	g/cc
81998	DK-252	2.65E-11	8.32E-12	1.31E+16	4.18E+16	9.05E-11	2.94	0.0154	8.86E-11	2.88	0.0153	8.67E-11	2.82	0.0155	7.88E-11	2.56	0.0704	0.279	1.03
62999	DK-252 + antioxidant	2.04E-11	8.94E-12	1.50E+16	3.41E+16	7.72E-11	2.86	0.0160	7.54E-11	2.79	0.0157	7.38E-11	2.73	0.0155	6.69E-11	2.48	0.1594	.0.318	
	AVERAGE	2.35E-11	8.63E-12	1.40E+16	3.79E+16	8.39E-11	2.90	0.0157	8.20E-11	2.84	0.0155	8.03E-11	2.78	0.0155	7.29E-11	2.52	0.1149		
82998	DK-502	1.98E-11	6.91E-12	1.56E+16	4.47E+16	7.95E-11	2.91	0.0140	7.80E-11	2.85	0.0134	7.66E-11	2.80	0.0134	7.03E-11	2.57	0.0614	0.314	1.03
83098	DK-502	2.31E-11	8.63E-12	1.50E+16	4.03E+16	8.70E-11	2.83	0.0143	8.53E-11	2.77	0.0135	8.38E-11	2.72	0.0134	7.65E-11	2.49	0.0651	0.279	1.04
70699	DK-502 + antioxidant	2.26E-11	8.44E-12	1.33E+16	3.57E+16	7.70E-11	2.89	0.0128	7.56E-11	2.84	0.0123	7.44E-11	2.79	0.0122	6.85E-11	2.57	0.0596	0.322	
	AVERAGE	2.18E-11	7.99E-12	1.47E+16	4.02E+16	8.12E-11	2.87	0.0137	7.96E-11	2.82	0.0131	7.83E-11	2.77	0.0130	7.17E-11	2.54	0.0620	0.297	1.04
81998	DK-582	1.71E-11	6.19E-12	2.06E+16	5.70E+16	9.00E-11	2.88	0.0126	8.84E-11	2.83	0.0129	8.69E-11	2.78	0.0136	7.92E-11	2.54	0.0696	0.275	1.03
70799	DK-582 + antioxidant	1.61E-11	7.14E-12	1.83E+16	4.12E+16	7.68E-11	2.95	0.0136	7.53E-11	2.90	0.0137	7.39E-11	2.84	0.0140	6.70E-11	2.58	0.1589	0.330	
	AVERAGE	1.66E-11	6.67E-12	1.94E+16	4.91E+16	8.34E-11	2.92	0.0131	8.19E-11	2.86	0.0133	8.04E-11	2.81	0.0138	7.31E-11	2.56	0.1143		
81998	DK-802	2.07E-11	7.52E-12	1.66E+16	4.57E+16	8.91E-11	2.93	0.0146	8.73E-11	2.87	0.0148	8.55E-11	2.81	0.0155	7.77E-11	2.55	0.0700	0.282	1.04
80599	DK-802 + antioxidant	2.43E-10	1.02E-10	1.21E+15	2.89E+15	7.70E-11	2.95	0.0130	7.56E-11	2.90	0.0133	7.42E-11	2.84	0.0137	6.81E-11	2.61	0.0606	0.329	
	AVERAGE	1.32E-10	5.48E-11	8.93E+15	2.43E+16	8.31E-11	2.94	0.0138	8.15E-11	2.88	0.0141	7.99E-11	2.83	0.0146	7.29E-11	2.58	0.0653		
82798	DK-812	1.66E-11	6.28E-12	1.87E+16	4.95E+16	8.13E-11	2.95	0.0155	7.95E-11	2.89	0.0157	7.78E-11	2.83	0.0169	7.08E-11	2.57	0.0653	0.312	1.04
72399	DK-812 +antioxidant	1.37E-11	4.97E-12	2.23E+16	6.14E+16	8.12E-11	3.01	0.0146	7.95E-11	2.95	0.0149	7.79E-11	2.89	0.0158	7.01E-11	2.60	0.1667	0.318	
	AVERAGE	1.52E-11	5.63E-12	2.05E+16	5.54E+16	8.12E-11	2.98	0.0151	7.95E-11	2.92	0.0153	7.78E-11	2.86	0.0164	7.05E-11	2.59	0.1160		
	XX2 SERIES AVG	4.18E-11	1.67E-11	1.55E+16	4.14E+16	8.25E-11	2.92	0.0143	8.09E-11	2.86	0.0142	7.93E-11	2.81	0.0147	7.22E-11	2.56	0.0945		
71999	DK-503	1.79E-11	6.37E-12	1.65E+16	4.63E+16	7.59E-11	2.91	0.0125	7.46E-11	2.86	0.0121	7.34E-11	2.81	0.0121	6.76E-11	2.59	0.0596	0.329	
72099	DK-503 (hand mixed)	1.76E-11	6.40E-12	1.47E+16	4.03E+16	6.77E-11	2.97	0.0130	6.65E-11	2.91	0.0126	6.54E-11	2.86	0.0126	6.06E-11	2.65	0.0550	0.376	
	AVERAGE	1.78E-11	6.39E-12	1.56E+16	4.33E+16	7.18E-11	2.94	0.0128	7.06E-11	2.89	0.0124	6.94E-11	2.84	0.0124	6.41E-11	2.62	0.0573		
72199	DK-504	1.21E-10	6.24E-11	2.44E+15	4.72E+15	7.64E-11	2.93	0.0122	7.51E-11	2.88	0.0119	7.39E-11	2.83	0.0119	6.81E-11	2.61	0.0587	0.329	
101999	DK-502NC	2.32E-11	8.52E-12	1.33E+16	3.63E+16	8.00E-11	2.93	0.0156	7.83E-11	2.86	0.0145	7.68E-11	2.81	0.0141	7.09E-11	2.59	0.0669	0.314	
102299	DK-502NC	2.28E-11	9.35E-12	1.35E+16	3.30E+16	8.17E-11	2.99	0.0156	8.00E-11	2.93	0.0145	7.84E-11	2.87	0.0142	7.07E-11	2.59	0.1642	0.314	
110899	DK-502NC	2.80E-11	1.05E-11	1.11E+16	2.97E+16	8.14E-11	2.96	0.0182	7.94E-11	2.90	0.0168	7.76E-11	2.84	0.0160	6.98E-11	2.59	0.1638	0.311	
	AVERAGE	2.47E-11	9.46E-12	1.27E+16	3.30E+16	8.10E-11	2.96	0.0165	7.92E-11	2.90	0.0153	7.76E-11	2.84	0.0148	7.05E-11	2.59	0.1316		0.00
	<u>Commercial Polyurethanes</u>																		
61898	Uralite 3125/3119	8.57E-09	6.67E-09	4.12E+13	5.29E+13	1.93E-10	6.18	0.0887	1.69E-10	5.41	0.0874	1.50E-10	4.81	0.0792	1.19E-10	3.81	0.1473	0.275	1.14
73098	Epoxies Etc. 20-2350	5.10E-10	4.70E-10	7.04E+14	7.64E+14	1.11E-10	3.50	0.0092	1.09E-10	3.43	0.0235	1.04E-10	3.26	0.0485	8.66E-11	2.73	0.1186	0.270	1.00
	<u>Epoxies</u>																		
80498	Formula 456	1.68E-11	7.86E-12	2.02E+16	4.30E+16	1.11E-10	3.71	0.0123	1.09E-10	3.66	0.0220	1.05E-10	3.51	0.0298	9.14E-11	3.06	0.0972	0.287	1.12
81098	Formula 459	4.05E-12	1.71E-12	8.40E+16	1.99E+17	1.12E-10	3.71	0.0107	1.09E-10	3.63	0.0199	1.06E-10	3.51	0.0267	9.36E-11	3.11	0.0987	0.285	1.16
81398	Standard Epon/Ver	7.06E-12	2.78E-12	4.89E+16	1.24E+17	9.29E-11	3.04	0.0076	9.15E-11	2.99	0.0136	8.95E-11	2.93	0.0173	8.06E-11	2.64	0.0730	0.281	1.14
81198	Reversed Epon/Ver	1.23E-09	9.00E-10	2.67E+14	3.65E+14	9.53E-11	3.27	0.0207	9.28E-11	3.19	0.0192	9.04E-11	3.11	0.0205	8.09E-11	2.78	0.0769	0.295	1.05

NOTE: Sample 2 indicates that a second test plaque was cut from the casting in the row above.

Table E-2. Electrical Tests at 200°F

Sample Date	Formulation	I: 1 min.	I: 3 min.	Vol. Res.: 1 min.	Vol. Res.: 3 min.	1 kHZ Cp	K	D	10 kHZ Cp	K	D	100 kHZ Cp	K	D	1000 kHZ Cp	K	D	Sample Thick.	den.
		Amps	Amps	ohm-cm	ohm-cm	Farads			Farads			Farads			Farads			cm	g/cc
21898	EN-7 (sample 2)	1.78E-08	1.67E-08	1.66E+13	1.77E+13	9.80E-11	3.74	0.0597	8.83E-11	3.37	0.0699	8.02E-11	3.07	0.0574	6.96E-11	2.66	0.0876	0.328	
43098	EN-7 (sample 2)	2.17E-08	2.11E-08	1.55E+13	1.59E+13	1.11E-10	3.74	0.0523	1.01E-10	3.40	0.0692	9.12E-11	3.07	0.0612	7.79E-11	2.62	0.0955	0.289	
	AVERAGE	1.98E-08	1.89E-08	1.60E+13	1.68E+13	1.04E-10	3.74	0.0560	9.46E-11	3.39	0.0696	8.57E-11	3.07	0.0593	7.38E-11	2.64	0.0916		
30498	Ato. B w/2143L (# 2)	1.13E-09	1.04E-09	2.60E+14	2.83E+14	8.92E-11	3.43	0.0335	8.45E-11	3.25	0.0389	7.99E-11	3.07	0.0378	7.04E-11	2.71	0.0828	0.330	
31898	Ato. B w/R1680 (# 2)	4.11E-09	3.49E-09	7.17E+13	8.45E+13	8.88E-11	3.40		8.51E-11	3.26		8.10E-11	3.11		7.17E-11	2.75		0.329	
41698	DK-251 (sample 2)	3.61E-09	3.04E-09	9.70E+13	1.15E+14	1.01E-10	3.26	0.0181	9.81E-11	3.16	0.0274	9.39E-11	3.03	0.0329	8.20E-11	2.65	0.0897	0.277	
33198	DK-501 (sample 2)	1.51E-08	1.33E-08	2.28E+13	2.59E+13	1.09E-10	3.57		1.03E-10	3.38		9.64E-11	3.17		8.29E-11	2.72		0.282	
40498	DK-581 (sam. 2)***	5.88E-08	5.77E-08	5.76E+12	5.88E+12	1.00E-10	3.34		9.57E-11	3.19		9.10E-11	3.03		8.01E-11	2.67		0.286	
32398	DK-801 (sample 2)	1.37E-09	1.28E-09	2.16E+14	2.31E+14	8.67E-11	3.31	0.0173	8.40E-11	3.21	0.0268	8.05E-11	3.07	0.0318	7.12E-11	2.72	0.0821	0.328	
40298	DK-811 (sample 2)	4.55E-09	3.65E-09	7.38E+13	9.19E+13	9.62E-11	3.24		9.38E-11	3.16		9.03E-11	3.04		7.95E-11	2.68		0.289	
	XX1 SERIES AVG	1.67E-08	1.58E-08	8.30E+13	9.40E+13	9.86E-11	3.34	0.0177	9.49E-11	3.22	0.0271	9.04E-11	3.07	0.0324	7.91E-11	2.69	0.0859		
81998	DK-252	4.39E-09	3.87E-09	7.92E+13	8.98E+13	1.05E-10	3.41	0.0255	1.00E-10	3.25	0.0331	9.55E-11	3.10	0.0348	8.36E-11	2.72	0.0893	0.279	1.03
82998	DK-502	2.86E-09	2.81E-09	1.08E+14	1.10E+14	9.52E-11	3.48	0.0447	8.90E-11	3.26	0.0448	8.38E-11	3.07	0.0391	7.40E-11	2.71	0.0831	0.314	1.03
83098	DK-502	5.04E-09	4.35E-09	6.90E+13	7.99E+13	1.06E-10	3.45	0.0448	9.91E-11	3.22	0.0468	9.30E-11	3.02	0.0417	8.11E-11	2.64	0.0892	0.279	1.04
70699	DK-502 + antioxidant	5.95E-09	4.88E-09	5.06E+13	6.17E+13	9.43E-11	3.54	0.0452	8.79E-11	3.30	0.0463	8.26E-11	3.10	0.0407	7.27E-11	2.73	0.0833	0.322	
	AVERAGE	4.62E-09	4.01E-09	7.59E+13	8.39E+13	9.86E-11	3.49	0.0449	9.20E-11	3.26	0.0460	8.65E-11	3.06	0.0405	7.59E-11	2.69	0.0852	0.297	1.04
81998	DK-582	3.25E-08	3.23E-08	1.09E+13	1.09E+13	1.02E-10	3.28	0.0305	9.74E-11	3.12	0.0328	9.32E-11	2.98	0.0301	8.24E-11	2.64	0.0825	0.275	1.03
81998	DK-802	2.92E-09	2.53E-09	1.18E+14	1.36E+14	1.03E-10	3.37	0.0240	9.84E-11	3.23	0.0319	9.38E-11	3.08	0.0335	8.24E-11	2.71	0.0874	0.282	1.04
82798	DK-812	4.80E-09	4.05E-09	6.48E+13	7.68E+13	9.06E-11	3.29	0.0191	8.76E-11	3.18	0.0259	8.43E-11	3.06	0.0281	7.51E-11	2.73	0.0800	0.312	1.04
		9.85E-09	9.36E-09	6.97E+13	7.95E+13	9.98E-11	3.37	0.0288	9.51E-11	3.21	0.0339	9.06E-11	3.06	0.0334	7.99E-11	2.70	0.0849		
71999	DK-503	3.45E-09	2.92E-09	8.54E+13	1.01E+14	9.17E-11	3.51	0.0437	8.57E-11	3.28	0.0447	8.07E-11	3.09	0.0394	7.13E-11	2.73	0.0816	0.329	
72199	DK-504	3.09E-09	2.66E-09	9.54E+13	1.11E+14	9.21E-11	3.53	0.0428	8.63E-11	3.31	0.0435	8.13E-11	3.12	0.0383	7.07E-11	2.71	0.1858	0.329	
101999	DK-502NC	8.55E-09	8.23E-09	3.61E+13	3.75E+13	9.67E-11	3.54	0.0414	9.06E-11	3.31	0.0459	8.49E-11	3.11	0.043	7.50E-11	2.74	0.0948	0.314	
102299	DK-502NC	9.20E-09	8.35E-09	3.36E+13	3.70E+13	9.92E-11	3.63	0.0425	9.27E-11	3.39	0.0467	8.68E-11	3.18	0.0435	7.42E-11	2.71	0.1949	0.314	
	AVERAGE	8.88E-09	8.29E-09	3.48E+13	3.73E+13	9.80E-11	3.58	0.0420	9.17E-11	3.35	0.0463	8.59E-11	3.14	0.0433	7.46E-11	2.73	0.1449		0.00
	<u>Commercial Polyurethanes</u>																		
61898	Uralite 3125/3119*	5.96E-06	5.96E-06	5.92E+10	5.91E+10	2.26E-10	7.24	0.0220	2.22E-10	7.11	0.0202	2.15E-10	6.89	0.0354	1.67E-10	5.35	0.1720	0.275	1.14
73098	Epoxies Etc. 20-2350	1.95E-08	1.86E-08	1.84E+13	1.93E+13	9.28E-11	2.92	0.0005	9.28E-11	2.92	0.0013	9.27E-11	2.92	0.0028	8.50E-11	2.67	0.0668	0.270	1.00
	<u>Epoxies</u>																		
80498	Formula 456	5.89E-09	3.50E-09	5.74E+13	9.66E+13	1.21E-10	4.05	0.0053	1.20E-10	4.02	0.0072	1.19E-10	3.98	0.0139	1.04E-10	3.49	0.0956	0.287	1.12
81098	Formula 459	6.06E-09	3.55E-09	5.62E+13	9.59E+13	1.23E-10	4.07	0.0064	1.21E-10	4.03	0.0073	1.20E-10	3.99	0.0129	1.05E-10	3.50	0.0944	0.285	1.16
81398	Standard Epon/Ver**	9.77E-09	8.35E-09	3.53E+13	4.13E+13	1.14E-10	3.74	0.0319	1.10E-10	3.60	0.0229	1.07E-10	3.51	0.0240	9.37E-11	3.07	0.0953	0.281	1.14
81198	Reversed Epon/Ver	1.02E-03	9.93E-06	3.22E+08	3.31E+10	2.35E-10	8.07	0.5716	2.14E-10	7.36	0.1203	1.90E-10	6.52	0.1256	1.30E-10	4.47	0.2375	0.295	1.05

* Turned from yellow to orange on heating

** Sample not flat and heated one hour with clamped electrodes to improve contact. Total heating time to measurement was 3 hours.

*** Heated 6 hours instead of 2.

Table E-3. Mechanical Tests

Sample Date	Formulation	Shore A Hardness (1/10 seconds)	Stress at 100%	Ultimate Elongation	Ultimate Strength	Tear Strength
		points	psi	percent	psi	ppi
21898	EN-7	92 / 90	1023±14	340±18	1673±84	373±9
43098	EN-7	92 / 90	937±18 (6)	357±39 (6)	1803±222 (6)	369±16
70899	EN-7	92 / 88	953±28 (6)	361±97 (6)	1455±247 (6)	366±12 (3)
	AVERAGE	92 / 89	971	353	1644	369
30498	AtoChem B with 2143L	82 / 78	629±16	175±30	919±165	206±19
31898	Atochem B with R1680	76 / 72	850±23	216±44	1488±196	240±41 (6)
41698	DK-251	70 / 65	464±12	255±42	1065±119	157±25 (6)
33198	DK-501	76 / 71	572±8	352±57	1314±98	212±20 (6)
41498	DK-581	78 / 75	751±22	170±24	1080±121	144±10
32398	DK-801	73 / 68	499±24	223±37	987±164	154±12 (6)
40298	DK-811	73 / 68	562±17	202±11	1019±103	169±4
81998	DK-252	81 / 76	1041±37 (4)	222± 28 (4)	1638±102 (4)	247±11
62899	DK-252 with antioxidant	82 / 76	888±40 (6)	221±44 (6)	1367±189 (6)	200±5 (3)
	AVERAGE	82 / 76	965	222	1503	224
82998	DK-502	88 / 84	1076±34	224±47	1697±307	396±22
83098	DK-502	NA	1097±38	262±30	1977±92	311±21 (6)
63099	DK-502 with antioxidant	87 / 84	1149±34 (6)	213±72 (6)	1798±436 (6)	357±19 (3)
	AVERAGE	88 / 84	1107	233	1824	355
101999	DK-502NC	84/	1011±63	295±38	1561±36	316±7
102299	DK-502NC	86/	1069±27	337±48	1899±66	381±16
110899	DK-502NC (fresh I-50/KF865)	82/	911±9	379±59	1653±95	307±6
	AVERAGE	84/	997	337	1704	335
81998	DK-582	84 / 81	1289±38	151±21	1818±215	205±31
70799	DK-582 with antioxidant	82 / 78	1272±41 (4)	143±17 (4)	1706±206 (4)	166±19 (3)
	AVERAGE	83 / 80	1281	147	1762	186
81998	DK-802	81 / 76	1037±32	218±28	1723±59	245±7
61799	DK-802 with antioxidant	83 / 80	1174±20 (4)	199±17 (4)	1772±79 (4)	235±12
	AVERAGE	82 / 78	1106	209	1748	240
82798	DK-812	91 / 89	1015±23	148±9	1106±14	199±11
72399	DK-812 with antioxidant	82 / 78	838±12 (4)	215±20 (4)	1022±13 (4)	169±5
	AVERAGE	87 / 84	927	182	1064	184
71999	DK-503	88 / 84	1337±59 (6)	247±29 (6)	1964±67 (6)	384±9 (3)
72099	DK-503 (hand mixed)	NA	1276±18	296±43	1629±16	321±10 (3)
	AVERAGE	88 / 84	1307	272	1797	353
72199	DK-504	88 / 84	1389±20 (4)	144±4 (4)	1596±29 (4)	352±20 (3)
61898	Uralite 3125/3119		1752±49	274±27	5755±697	505±9
73098	Epoxies Etc. 20-2350		78±23 (2)	118±1 (2)	116± 8 (2)	22±3
81198	RR Epon/Versamid		870±33	139±12	1134±81	184±9

Hardness average based on four measurements of stack of four disks with fresh top disk for each measurement.
Tensile and tear strength averages based on 5 samples unless otherwise noted in ().

Table E-4. Adhesive Tests

Sample Date	Formulation	Shear Stress	Thickness	Samples Tested
		psi	inches	
70899	EN-7	1161 ± 168	0.0021 ± 0.0011	4
62899	DK-252 with antioxidant	490 ± 57	0.0019 ± 0.0009	4
63099	DK-502 with antioxidant	1361 ± 337	0.0022 ± 0.0006	5
70799	DK-582 with antioxidant	491 ± 55	0.0026 ± 0.0011	4
61799	DK-802 with antioxidant	471 ± 49	0.0018 ± 0.0005	4
72399	DK-812 with antioxidant	400 ± 32	0.0009 ± 0.0005	4
71999	DK-503	971 ± 104	0.0025 ± 0.0009	4
72199	DK-504	721 ± 41	0.0031 ± 0.0015	4

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