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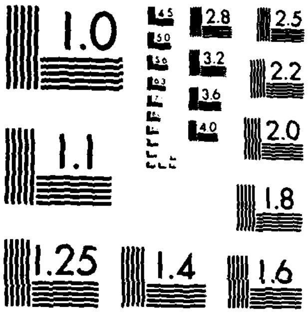

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DEVELOPMENT OF CASTOR OIL RESISTANT URETHANE SONAR ENCAPSULANTS

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Preparation and Evaluation of Castor Oil Resistant Polyurethane Encapsulants for Sonar Transducers.

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

A detailed development program was completed on new liquid castable polyurethanes suitable for the encapsulation of castor oil filled sonar transducers. The urethane encapsulants were designed to have improved castor oil resistance, be free of MBOCA [methylene bis (2-chloroaniline)] and consist of readily identifiable and available non-proprietary raw materials.

The systems of choice were found to be commercially available polyether urethane polymers based upon toluene diisocyanate/polyoxytetramethylene glycol and three

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SUMMARY

A detailed development and evaluation program has been completed on new MBOCA, methylene bis(2-chloroaniline), free polyurethane casting compounds suitable for the encapsulation of sonar transducers. The prime goals of the program were to develop urethane encapsulants of the following nature:

1. Improved Castor Oil resistance
2. MBOCA free
3. Non-proprietary components

This task was to be accomplished without undue reduction in other general handling and performance properties accepted as today's industry criteria.

Prototype liquid curing agents were prepared in which seven potential MBOCA substitutes were successively incorporated and evaluated. All but three of the new diamine curatives were eliminated from further consideration for one of the following reasons:

1. Withdrawn from commercial market.
2. Poor solubility such that room temperature stable liquid curing agents were not possible.
3. Severe incompatibility in the cured elastomer.
4. The cured urethanes were not transparent to visible light.

The three diamine curatives found to meet acceptance criteria were Polycure 1000, Cyanacure and Permapol D-562. Of these, Polycure 1000 and Permapol D-562 were the best. Cyanacure was the least attractive because of marginal liquid curing agent stability, and lower water and castor oil resistance of the cured urethanes.

Commercially available polymers based upon toluene diisocyanate/polyoxytetramethylene glycol (TDI/PTMG) proved to be the systems of choice. Urethane polymers having polyoxypropylene glycol (PPG) backbone structures were judged unacceptable because of high sound speeds or low mechanical properties. The diphenylmethane diisocyanate (MDI) analogues of TDI/PTMG based polymers were rejected due to poor container stability and short application lives with the various liquid curing agents. Adiprene L-100, L-167 and L-200 were selected for the final evaluation phase of the program. Adiprene L-167 with either Polycure or Permapol curing agents afforded the best overall balance of handling, mechanical, electrical and acoustical properties. Modest improvement in encapsulant electrical resistivity and insulation resistance was obtained by replacing Adiprene with Vibrathane polymers manufactured by Uniroyal Chemical. Elastomer sound velocity should remain unchanged with this substitution.

The water and castor oil resistances of the TDI/PTMG systems described above measured by changes in Shore A hardness and moduli over time at 122°F should meet the desired NRL requirement. Moduli at 100%, 200% and 300% extension changed by less than 25% during the accelerated exposure. General electrical performance properties, while somewhat lower than stated for commercial urethane systems based upon hydroxy terminated polybutadiene, should be acceptable as a sonar encapsulant for components containing castor oil as a fill fluid.

PREFACE

This final report covers work performed on Contract Number N00014-81-C-2576 during the period 12 October 1981 through 1 October 1982. The work was conducted in the Research and Development Laboratories of Products Research & Chemical Corporation located in Burbank, California.

The program was sponsored by Naval Research Laboratory. Technical liaison and sound velocity data were supplied by Dr. Corley M. Thompson of the Underwater Sound Reference Detachment, Naval Research Laboratory, Orlando, Florida.

The program was under the general direction of Mr. Lester Morris, Corporate Research Director, Products Research & Chemical Corporation. Technical efforts were conducted by Mr. W.T. Maurice, Program Manager and Mr. A. Reyes, Chemist, both of Products Research & Chemical Corporation.

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INTRODUCTION

A wide variety of elastomers such as neoprene, butyl and polyurethanes are employed in the fabrication of underwater sonar devices. The sonar system must operate over wide ranges in temperature, pressure and sound frequency in both salt and fresh water. In order to adequately perform this task, the sonar device must be encapsulated with some elastomeric material capable of protecting it not only from water ingress, but also from potentially corrosive vapors and fluids, abrasion, and mechanical and vibrational shock.

High performance liquid castable polyurethane electrical potting and molding compounds have been successfully empolyed as sonar transducer encapsulants for over twenty years. In general these materials have performed very well as the velocity of sound through the polyurethane is close to that through sea water. In some instances the sonar transducer may contain a fill fluid which is in long term contact with the encapsulant. A potential problem arises when the encapsulant is a polyurethane and the fill fluid is castor oil. Most polyurethanes in service today do not exhibit the desired level of long term castor oil resistance.

Department of the Navy has expressed concern over reported field failures of certain types of sonar transducer units. In the case of polyurethanes several modes of failure have been identified. These are apparent encapsulant failure due to water permeation at high service temperatures and attack of fill fluids, such as castor oil, on the encapsulant. These situations may also lead to adhesion loss between encapsulant and other component substrates ultimately resulting in electrical and/or acoustical failure of the transducer.

The Navy is also concerned over the possibility of encapsulant suppliers changing their basic raw material composition without first informing the proper government authority. The modified encapsulant may well meet all handling and performance criteria required by military specification, but ultimately fail somehow during service. This occurs in part, because not all of the critical performance characteristics are fully understood, and hence they cannot be adequately defined in the military specification which covers the encapsulant. As a result, this program was designed to develop new polyurethane sonar encapsulants possessing improved castor oil resistance from readily available commercial raw materials.
NRL set forth the following compositional, handling and performance requirements for the urethane encapsulant.

1. Non-proprietary individual components.
2. Encapsulant must be free of all potentially carcinogenic and hazardous components.
3. 30 minute minimum application life at 22°C.
4. 200 poise initial mixed viscosity at 25°C.
5. Gel time of 45-90 minutes at temperatures between 25° and 90°C.
6. 8 hour full cure at temperatures between 25° and 90°C.
7. The Shore A hardness should fall between 45 and 80, with 65 to 75 Shore A being the most desirable.
8. A minimum tensile strength of 2000 psi.
9. A minimum volume resistivity of 1.0×10^{12} ohm-cm.

10. A minimum dielectric strength of 300 KV/cm.

11. A glass transition temperature below -30°C.

12. The cured elastomer should yield a cohesive failure to primed mild steel.

13. The water vapor permeation constant should not exceed 1.0×10^{-7} gm-cm/cm^2-hr-torr. Testing to be conducted by NRL.

14. The product of sound speed x density within 10% of 1.6×10^6 Kg/M^2-sec. Testing to be conducted by NRL.

15. The acoustic attenuation between 1 KHz and 50 KHz must be less than 1dB/cm. Testing to be conducted by NRL.

16. The material must be transparent to visible light in 1 cm thickness.

17. Shear or Young's modulus must not change by more than 25%, or volume resistivity by more than 90% after a 2 year equivalent of water immersion. (Shear or Young's modulus was amended to stress-strain curve analysis by joint agreement between NRL and Products Research and Chemical Corp.)

18. Shear or Young's modulus must not change by more than 10% after a 2 year equivalent of castor oil immersion. (Shear or Young's modulus was amended to stress-strain curve analysis by joint agreement between NRL and Products Research and Chemical Corp.)

19. The formulation cost should not exceed $11.00/Kg ($5.00/lb.).

In addition, the contractor has supplied both a material process and material performance specification on the resulting sonar encapsulant.

INTERIM SYSTEM SCREENING

Initial screening tests were conducted with Adiprene L-100 and three similiar commercial polyether urethane prepolymers from PRC. These polymers were evaluated against four experimental liquid diamine/hydroxyl containing curing agents. The results of this work are summarized in Tables I and II. The selection of optimum stoichiometry is important with a high performance castable polyurethane. Normally, if one is using a diamine to cure an isocyanate terminated polymer, optimum properties will be obtained employing a weight mixing ratio in which the equivalent ratio of isocyanate to diamine is between 1.05-1.10/1.0. If the curing agent is composed of only hydroxyl containing reactants the equivalent ratio of isocyanate to hydroxyl normally runs between 0.95-1.05/1.0. In this program, where the urethane curing agents were composed of both amino and hydroxyl functions, mixing ratios were chosen to give an equivalent ratio of isocyanate to diamine plus hydroxyl of 1.05/1.0. In all instances throughout the program, the urethane elastomers were cured 16 hours at 180°F unless otherwise stated.

Urethane elastomers derived from experimental curing agent 64 proved to be of little interest because of low tensile strength and ultimate elongation. Elastomers prepared from experimental curing agents 78, 90 and 92 were too high in Shore A hardness for a suitable transducer encapsulant and not investigated further.

TABLE I
FIRST PHASE SYSTEM EVALUATION
MECHANICAL PROPERTIES

	Application Life (Time to 2500 Poise)	Hardness* (Shore A)	Tear Strength (Lbs/Inch)	Tensile Strength (PSI)	Ultimate Elongation (%)
1. PRC Permapol U-84 (5% available isocyanate, 91 poise) XCA **					
64	>3 hours	53	110	685	370
78	>2 hours	74	200	2500	700
90	>2 hours	66	150	850	500
92	>1.5 hours	68	190	1600	550
2. PRC Permapol U-82 (5% available isocyanate, 223 poise) XCA					
78	2 hours	83	310	3500	575
92	>2 hours	79	245	2120	460
3. PRC Permapol U-56 (7.1% available iscoyanate, 103 poise) XCA					
78	2 hours	84	310	3700	520
92	2 hours	79	250	2750	425
4. DuPont Adiprene L-100 (4.1% available isocyanate, 241 poise) XCA					
78	2 hours	78	250	3700	575
92	2 hours	77	260	4700	525

*Samples cured 16 hours at 180°F.
**Experimental Curing Agent

TABLE II
FIRST PHASE SYSTEM EVALUATION
ELECTRICAL PROPERTIES

	Resistivity at 75°F		Electrical Insulation Resistance
	Volume (ohm-cm)	Surface (ohms)	(megohoms)
1. PRC Permapol U-84			
XCA *			
64	5.5×10^{12}	9.3×10^{12}	275,000
78	8.3×10^{12}	1.9×10^{13}	358,000
90	1.7×10^{13}	6.0×10^{13}	415,000
92	3.4×10^{13}	5.1×10^{13}	405,000
2. PRC Permapol U-82			
XCA			
78	7.8×10^{12}	2.2×10^{13}	388,000
92	9.1×10^{12}	4.7×10^{13}	395,000
3. PRC Permapol U-56			
XCA			
78	6.6×10^{12}	1.7×10^{13}	349,000
92	8.6×10^{12}	2.2×10^{13}	377,000
4. DuPont Adiprene L-100			
XCA			
78	8.7×10^{11}	7.3×10^{12}	243,000
92	5.6×10^{12}	1.1×10^{13}	317,000

*Experimental Curing Agent

The experimental curing agent 78/Adiprene L-100 combination gave a volume resistivity which was 0.89 decades or factors of ten lower than the same curing agent with Permapol U-82 polymer. The electrical insulation resistance of the Adiprene system was 37% lower than that of Permapol U-82. Consider experimental curing agent 92 with Adiprene L-100 and Permapol U-84. The Adiprene material afforded a 0.83 decade lower volume resistivity and a 22% lower electrical insulation resistance than the U-84 polymer. The Adiprene polymers are based upon polyoxytetramethylene glycol and the two Permapol U polymers on polyoxypropylene glycol. We attribute the significant difference in electrical properties to the raw materials used in the manufacture of the polymers. We have found similar polymers based upon PTMG from Uniroyal Chemical give higher initial resistivity properties than Adiprene polymers.

NEW POLYMER SYNTHESIS

One portion of our original program proposal recommended investigation of new urethane polymer preparation in which the polymer backbone structure was composed of hydroxy terminated polybutadiene (HPBD) along with polyoxyproplyene and/or polyoxytetramethylane glycols. We believed, that if the resulting isocyanate terminated polymers were compatible, it might be possible to combine the hydrophobicity, electrical and acoustical properties of HPBD systems with the lo temperature flexibility, high tensile strength and oil resistance of the polyeth based urethanes. Six random copolymers, in which the major component was hydrox terminated polybutadiene (R45-HT), were prepared from 425 molecular weight polyoxypropylene glycol and 650 molecular weight polyoxytetramethylene glycol. Isocyanate end termination was achieved with Desmodur W, methylene bis (4-cyclohexylisocyanate), and IPDI (3-isocyanatomethyl-3,5,5-trimethylcyclohexyl-isocyanate). Polymer viscosities ran between 180-820 poise with available isocyanate contents of 5.5-6.3%. Compatibility was good with the PPG systems and marginal with the HPBD/PTMG materials.

The polymers were cured with a polyol curative especially formulated for polybutadiene systems. Hardnesses ran 50-60 Shore A, which is at the low end of our desired hardness range. Tear strengths, tensile strengths and ultimate elongations were 45-77 lb/in, 140-655 psi, and 265-650% respectively. These initial values were considered too low for a suitable sonar encapsulant. This effort was not continued because concurrent investigations by both NRL and Products Research disclosed the lack of acceptable castor oil resistance of commerically available HPBD based urethane encapsulants.

EVALUATION OF COMMERCIAL POLYMERS

Evaluation of commercially available urethane polymers included polyether urethanes derived from PPG (polyoxypropylene glycol) and PTMG (polyoxytetramethylene glycol). Polyether urethanes were selected because we believed they would come the closest to providing the desired level of castor oil resistance. Urethane polymers based upon HPBD (hydroxy terminated polybutadiene) were not included in this study because they are apparently not commercially available and both NRL and PRC had established earlier that urethane elastomers derived from HPBD do not possess the desired level of castor oil resistance.

One of the prime requisites of the program was to develop a material affording significantly higher castor oil resistance than is provided by urethanes currently in use. We believe most of the sonar encapsulants currently used are either PPG or HPBD based. PTMG urethanes have generally been neglected for this application because they form crystalline solids at 65°F or below, their tendency towards opaque products upon curing, and their formation of high Shore A hardness products when cured with MBOCA. If only castor oil resistance is considered, the PTMG systems should theorectically yield a higher level of resistance than either PPG or HPBD urethanes. Consequently, our basic emphasis was to investigate commercially available PTMG based polymers and certain PPG based polymers which we felt would give better castor oil resistance provided suitable curing agent technology could be developed.

CURING AGENT DEVELOPMENT

NRL had specified MBOCA, methylene bis(2-chloroaniline), free systems. Hence, MBOCA substitutes were chosen from those commercially available in mid 1981. These were:

1. Polycure 1000: methylene bis(methylanthranilate)
   PTM & W Industries Inc.
2. Polycure 1001: a low melting derivative of Polycure 1000
   PMT & W Industries Inc.
3. Polacure 740M: trimethylene glycol di-p-aminobenzoate
   Polaroid Corportation.
4. Cyanacure: 1,2-bis(2-aminophenylthio)ethane
   American Cyanamid
5. Permapol D-562: A low melting derivative of methylene bis (methylanthranilate)
   Products Research & Chemical Corporation
6. Apocure 601P: liquid version of Cyanacure
   M&T Chemicals
7. Baytec PU-1604: isobutyl 4-chloro-3,5-diaminobenzoate
   Mobay Chemical Co.

One of the major goals of the program was to develop an easily useable liquid castable urethane. This involves development of a liquid curing agent, or one which is easily converted into a suitably stable liquid composition. All of the currently known MBOCA substitutes are solids. Hence, combinations or solutions with isocyanate reactive liquid components were employed to obtain a suitable viscosity liquid curing agent. Inert liquid plasticizers are not acceptable in high performance urethanes as they tend to migrate under service conditions and disrupt adhesion. Liquid components were selected which maintain a good balance between diamine solubility, low viscosity, and system compatibility, while providing reasonable handling and performance characteristics in the end products.

It was found very early into the task that all the proposed MBOCA substitutes under investigation lack to varying degrees the desirable solubility characteristics of MBOCA in liquid isocyanate reactive curing agent components. Good diamine solubility in the other curing agent components is necessary to obtain optimum compatibility in the cured urethane elastomer. Experience in developing liquid castable polyurethanes has shown that general mechanical properties improve with increasing cured elastomer compatibility. Compatibility in the cured products is also necessary to attain an encapsulant which will allow visual inspection of the completed sonar device. Incompatible systems will result in cured urethane elastomers which are translucent or even opaque to visible light. They may also afford elastomers with less than optimum performance properties. Extensive effort was devoted to finding compositions which approached acceptable diamine solubility.

The first curing agent which showed promise is listed below:

Component	Supplier	Parts by Weight (%)
2-ethyl-1,3-hexanediol	Union Carbide	14.70
N,N-(2-hydroxypropyl) aniline	Upjohn Co.	36.75
Diamine Component	(See page 6)	22.05
N,N,N',N'-tetrakis-(2-hydroxy-propyl) ethylenediamine or (Quadrol)	BASF Wyandotte	26.46
Ferric Acetonyl Acetonate	Harshaw Chemical	0.04
		100.00

This basic curing agent formula was selected so that the resulting cured urethane elastomers were within the desired hardness range, were flexible but not thermoplastic, and were suitably compatible. This involves obtaining, through a combination of theoretical and experimental considerations, an optimum balance between the chemical equivalence of curing agent difunctional and polyfunctional components. Each of the seven diamine curatives were substituted directly into the formula at 22.05 weight percent. All of the curing agent compositions remained homogeneous liquids for at least 8 to 11 hours at ambient temperature.

Catalyst selection plays a key role in handling and appearance of castable urethanes. Organo tin compounds such as dibutyl tin dilaurate or the diacetate derivative afforded optically clear elastomers. They were not satisfactory in this curing agent as the elastomers were prone to gassing due to moisture or water sensitivity. Internal stress cracking also developed during elevated temperature cures. Tin catalysts are used in high performance castable urethanes, but each individual system must be evaluated as the tin derivatives may act to catalyze gas formation reactions yielding a foam as well as catalyze reactions to form elastomers.

Lead naphthenate, oleate and octoate eliminated water sensitivity and stress cracking but gave end products with poor compatibility. These lead salts of organic acids afforded cured urethanes which were either translucent or opaque to visible light. Polymers based upon a PPG backbone were translucent, while those containing a PTMG backbone were opaque. Tertiary amine catalysts were not investigated because their activity is primarily directed towards the isocyanate-water reaction rather than the desired isocyanate-hydroxyl reactions. These same amines may also be electrically conductive and/or corrosive in the presence of water.

The best catalyst in terms of activity, compatibility, and long term package stability was found to be FeAA (ferric acetonyl acetonate). Other chelates such as cobalt AA or manganese AA had too low a level of activity to be practical. Iron carboxylates such as the naphthenate and tallate were found to be good overall catalysts, but final products tended to be opaque.

Sixteen hour 180°F cures were conducted using a low and medium viscosity urethane polymers based upon TDI/PPG. The data is summarized in Tables III and IV. Additional work is also shown in Table V with PTMG based polymers Adiprene L-100 and L-167.

All the materials shown in Tables III and IV have desirable mixed viscosities, long application lives, and excellent volume and surface resistivities. The hardnesses, tear strengths, tensile strengths, and ultimate elongations are all low. In contrast, the materials shown in Table V have excellent electrical resistivities, tear and tensile strengths, but hardness is too high and elongations too low.

The PTMG based elastomers shown in Table V are an improvement over the PPG based elastomers shown in Tables III and IV, but the ultimate elongations remain low. One interesting note. The electrical resistivities of the Permapol U-47 based elastomers are much higher than those of the Adiprene L-167 systems.

We attempted to improve ultimate elongation by two means. The first was to increase the diamine content of the curing agent. This technique will generally raise elongation, tensile, tear and hardness. This arises because the equivalent ratio of diamine to tri- and/or tetrafunctional hydroxyl is increased. In this instance, when the diamine level was raised from 22 to 36 weight percent, the resulting curing agents were no longer stable liquids. Crystalline diamine rapidly came out of solution upon standing at ambient temperature. The worst case was Polacure 740 M. It crystallized after 2 hours room temperature conditioning. Lesser amounts of diamine did not suitably increase elongation. Based on experience, a practical liquid curing agent must be physically stable for a minimum of 8 hours at ambient temperatures after liquefying from a solid or semi-solid state.
The second approach was to modify the curing agent by reducing the chemical equivalent ratio of polyfunctional hydroxyl to difunctional hydroxyl. This must be accomplished while retaining a reasonable level of diamine solubility. The initial attempts involved replacing a portion of the Quadrol with trifunctional castor oil, and replacing a portion of the ethylhexane diol with 1500 equivalent weight, TDI extended polyether diol. We were able to increase the ultimate elongation from 250-300% up to 380%. The curing agents remained liquids, but their individual viscosities were too high at 960-1000 poise to be acceptable. Therefore, both means attempted to improve ultimate elongation could not be used.

TABLE III
DIAMINE CONTAINING CURING AGENTS WITH PERMAPOL U-84 URETHANE POLYMER*

Diamine Component	Polycure 1000	Polycure 1001	Apocure 601P	Cyanacure	Polacure 740M	Baytec PU-1604	Permapol D-562
Mixed Viscosity (poise at 75°F)	220	180	160	150	180	160	180
Application Life, minutes (time to 2500 poise)	300	240	240	240	240	300	300
Hardness (Shore A)	44	45	44	45	44	45	44
Tensile Strength (PSI)	340	355	320	475	218	370	350
Ultimate Elongation (%)	325	310	350	300	300	300	300
Tear Strength (lbs/in.)	53	62	46	55	38	51	59
Resistivity at 75°F							
Volume (ohm-cm)	6.3×10^{11}	5.8×10^{11}	3.1×10^{12}	9.9×10^{12}	9.4×10^{12}	3.0×10^{12}	8.6×10^{11}
Surface (ohms)	9.9×10^{12}	6.8×10^{12}	7.9×10^{13}	9.6×10^{13}	1.1×10^{14}	9.1×10^{13}	1.3×10^{13}
Elastomer Color, Clarity	Clear, light amber	Clear, light amber	Clear, light amber	Clear, light amber	Clear, light amber	Clear, very dark	Clear, light amber

*A 5% available isocyanate polymer based upon TDI and PPG polyethers (206 poise viscosity). Products Research and Chemical Corporation.

TABLE IV
DIAMINE CONTAINING CURING AGENTS WITH PERMAPOL U-47 URETHANE POLYMER*

Diamine Component	Polycure 1000	Polycure 1001	Apocure 601P	Cyanacure	Polacure 740M	Baytec PU-1604	Permapol D-562
Mixed Viscosity (poise at 75°F)	320	260	220	290	320	300	300
Application Life, minutes (time to 2500 poise)	85	70	30	45	40	60	65
Hardness (Shore A)	97	98	96	98	99	98	98
Tensile Strength (PSI)	4670	4030	4775	3950	4850	4875	4440
Ultimate Elongation (%)	250	250	250	250	250	250	250
Tear Strength (lbs./in.)	480	405	485	345	545	490	469
Resistivity at 75°F Volume (ohm-cm)	8.2×10^{13}	5.1×10^{13}	2.2×10^{15}	3.7×10^{14}	$>1\times10^{16}$	4.6×10^{15}	7.2×10^{13}
Surface (ohms)	1.4×10^{14}	2.7×10^{14}	3.1×10^{15}	2.0×10^{15}	$>1\times10^{16}$	4.8×10^{15}	3.6×10^{14}
Elastomer Color, Clarity	Clear, medium amber	Clear, medium amber	Clear, medium amber	Clear, medium amber	Clear, medium amber	Opaque, very dark	Clear, medium amber

*A 8.8% available isocyanate polymer based upon TDI and PPG polyethers (91 poise viscosity). Products Research and Chemical Corporation.

TABLE V
POLACURE 740M CONTAINING CURING AGENT WITH ADIPRENE L-100 AND L-167 URETHANE POLYMERS*

	Adiprene L-100	Adiprene L-167
Mixed Viscosity (poise at 75°F)	288	202
Application Life, minutes (time to 2500 poise)	194	62
Hardness (Shore A)	58	84
Tensile Strength (PSI)	2715	4470
Ultimate Elongation (%)	315	275
Tear Strength (lbs./in.)	285	485
Resistivity at 75°F		
Volume (ohm-cm)	2.3×10^{12}	3.6×10^{12}
Surface (ohms)	4.8×10^{13}	4.1×10^{13}
Elastomer Color, Clarity	Clear, medium amber	Clear, medium amber

*L-100, 4.08% available isocyanate (233 poise).
L-167, 6.18% available isocyanate (88 poise).

During this period we were informed by M&T Chemicals that Apocure 601P was no longer a commercial product. It was deleted from further work in the program. Of the remaining six diamine curatives, Polycure 1000, Polycure 1001 and Permapol D-562, all afforded nearly equivalent performance properties. This fact may be confirmed by a review of Tables III and IV. The most noteworthy feature between the three is the significantly higher curing agent solubility of the Permapol material. We were unable to find any difference between the two Polycures except that PC-1001 gave somewhat inferior elastomers compared to the PC-1000. Thus, Polycure 1000 and Permapol D-562 were retained for further study. We subsequently learned that Polycure 1001 is no longer commercially available.

The low elastomer elongations and high curing agent viscosities were ultimately overcome by replacing the Quadrol and 1500 equivalent weight PTMG diol with castor oil and a very low viscosity 2000 molecular weight PPG diol. This had the overall effect of changing the chemical equivalent ratio of tetrol/diol from 0.655/1.0 down to a 0.244/1.0 triol/diol ratio. This modification amounted to a 62% reduction in curing agent hydroxyl functionality.

Subsequent work to further refine the curing agent composition afforded no improvement in properties. If castor oil was replaced with various molecular weight PPG triols, diamine solubilities were disproportionally reduced. If the castor oil content was increased much beyond 31 weight percent, diamine solubility decreased. Diamine solubility was found in the following order:

Baytec = Permapol > Polycure > Cyanacure > Polacure

The new curing agent composition, which ultimately was shown to be optimum is presented below:

Component	Supplier	Parts by Weight (%)
2-Ethyl-1,3-hexanediol	Union Carbide	6.02
N,N-(2-hydroxypropyl)aniline	Upjohn Co.	18.07
Diamine component	(See page 6)	21.68
Castor Oil	Caschem	24.09
2000 PPG diol	Olin Corp.	30.11
Ferric acetonyl acetonate	Harshaw Chemical	0.03
		100.00

This basic curing agent composition afforded viscosities in the 38-42 poise range which is highly desirable. We were able to incorporate all diamine curatives successfully save for Polacure 740M. The curing agent containing Polacure 740M readily crystallized upon cooling to 120°F, and did not yield a room temperature stable liquid. The Polacure 740M concentration had to be reduced from 21.6% down to an unacceptable 14.5% before a stable liquid curing agent could be obtained.

The elastomers resulting from the reduced Polacure concentration were inferior in cured physical properties to the remaining diamines used at the higher concentration. Polacure 740M was therefore dropped from further consideration. Polacure afforded good elastomers which gave excellent electrical properties as can be seen from the data presented in Tables III, IV and V. Nonetheless, most high strength castable polyurethanes which employ diamine containing curing agents will require some preprocessing of that curing agent. Consequently, the curing agent which after decrystallization remains liquid the longest is potentially the most trouble-free. We ran long-term crystallization studies at 73-76°F on the remaining curing agents. The results are summarized as follows:

Curing Agent	Aging Characteristics at 73-76°F
Polycure 1000	Crystallized after 16 hours
Cyanacure	Crystallized after 8 hours
Baytec PU-1604	Remained homogeneous liquid after 3 weeks exposure
Permapol D-562	Remained homogeneous liquid after 3 weeks exposure

As stated previously a curing agent suitable for field use should remain in a liquid state for a minimum of 8 hours at ambient temperatures. This minimum period allows for curing agent decrystallization and cool down prior to use. Under this criterion, the Cyanacure diamine formula would be only marginally acceptable, but because its basic performance properties were good, it was retained in the program.

SCREENING OF CANDIDATE ELASTOMERS

The remaining four curing agents were employed as curatives for TDI/PTMG, TDI/PPG and MDI/PTMG based polymers. The resulting data are summarized in Tables VI, VII, VIII and IX.

Urethane elastomers based upon Adiprene L-200 exhibit very low initial mixed viscosities, long application lives and quite acceptable hardnesses, tears, tensiles and ultimate elongations. The L-200 systems yield slightly higher electrical properties than either L-100 or L-167. In terms of mechanical and electrical properties, the Baytec containing curing agents gave the best results followed by Polycure, Permapol and Cyanacure.

Cyanacure and the now deleted Polacure 740M gave the best results electrically. This is evidenced by volume and surface resistivity data of Tables IV, V and VI, and the insulation resistance data of Table VI. The resistivities can be raised a full decade by changing to a PPG based polymer from the TDI/PTMG types. Tear strength, and tensile strength are all lower with the PPG systems. This is substantiated by comparing the data of Table VI to Table VII.

NRL imposed one very important criterion on the candidate sonar encapsulant. It must be transparent to visible light. Our own experience with present day sonar encapsulants, is that they are almost always a clear, or slightly translucent, lightly colored material. The transparency is necessary because the final component is subjected to visual inspection. This aspect is important as the transducer must be free from air bubbles, foreign matter, and other imperfections, which if present, will generally induce some form of signal attenuation.

At this point in the development, Baytec PU-1604 would have been the choice as a MBOCA substitute for sonar applications as well as general polyurethane potting and molding operations. Unfortunately, it has one serious drawback which could not be overcome by curing agent modification. The Baytec cured polyether urethanes are either exceptionally dark or opaque. The best compatibility is achieved with PPG based polymers, the worst with PTMG derived polymers. Baytec PU-1604 was therefore eliminated from further consideration.

Initial efforts to match the mechanical properties of the TDI/PTMG polymers with those containing a PPG backbone were unsuccessful. Permapol U-47 is a non-crystallizing, high strength TDI/PTMG based urethane polymer which meets and exceeds the basic performance properties of the three TDI/PTMG systems included in this program. This is confirmed by comparing the data of Table IX to that of Table VI. The electrical properties are in fact a full decade higher.

TABLE VI
FINAL SCREENING TEST OF DIAMINES WITH TDI/PTMG POLYMERS

	Polycure 1000	Cyanacure	Baytec PU-1604	Permapol D-562
Mixed Viscosity (poise at 75°F)				
L-100	350	380	380	250
L-167	110	120	90	70
L-200	90	115	110	110
Application Life, Hrs. (time to 2500 poise)				
L-100	7	7	7	7
L-167	7.5	7	7	7
L-200	7	7	7	7
Hardness (Shore A)				
L-100	67	53	73	64
L-167	70	55	82	68
L-200	78	65	87	74
Tensile Strength (PSI)				
L-100	3280	1375	1805	2815
L-167	3255	1340	2130	2585
L-200	3123	2560	2695	2765
Ultimate Elongation (%)				
L-100	630	600	800	600
L-167	600	600	775	550
L-200	500	500	600	500
Tear Strength (lbs./in.)				
L-100	178	87	172	153
L-167	187	105	244	143
L-200	205	150	295	185
Resistivity at 75°F				
Volume/Surface (ohm-cm/ohms)				
L-100	$1.7\text{x}10^{10}$/ $3.4\text{x}10^{11}$	$4.7\text{x}10^{10}$/ $1.3\text{x}10^{12}$	$4.3\text{x}10^{10}$/ $5.1\text{x}10^{11}$	$2.2\text{x}10^{10}$/ $4.2\text{x}10^{11}$
L-167	$3.1\text{x}10^{10}$/ $5.4\text{x}10^{11}$	$1.5\text{x}10^{11}$/ $5.7\text{x}10^{12}$	$1.3\text{x}10^{11}$/ $3.7\text{x}10^{12}$	$4.8\text{x}10^{10}$/ $7.9\text{x}10^{11}$
L-200	$9.3\text{x}10^{10}$/ $1.4\text{x}10^{12}$	$3.8\text{x}10^{11}$/ $1.2\text{x}10^{13}$	$2.3\text{x}10^{11}$/ $5.7\text{x}10^{12}$	$1.1\text{x}10^{11}$/ $2.1\text{x}10^{12}$

TABLE VI (Continued)
FINAL SCREENING TEST OF DIAMINES WITH TDI/PTMG POLYMERS

	Polycure 1000	Cyanacure	Baytec Pu-1604	Permapol D-562
Insulation Resistance (megohms at 75°F)				
L-100	1.6×10^3	3.8×10^3	7.2×10^3	1.2×10^3
L-167	3.8×10^3	8.2×10^3	9.8×10^3	7.9×10^3
L-200	1.3×10^3	5.1×10^4	3.3×10^4	1.6×10^4
Elastomer, Color, Clarity				
L-100	Medium amber, Clear	Light amber, Clear	Very dark, Opaque	Medium amber, Clear
L-167	Medium amber, Clear	Light amber, Clear	Very dark, Opaque	Medium amber, Clear
L-200	Medium amber, Clear	Light amber, Clear	Very dark, Opaque	Medium amber, Clear

TABLE VII
DIAMINE CONTAINING CURING AGENTS WITH PERMAPOL U-56*

Diamine Component	Polycure 1000	Cyanacure	Baytec PU-1604	Permapol D-562
Mixed Viscosity (poise at 75°F)	100	90	110	99
Application Life, Hrs. (time to 2500 poise)	7	7	7	7
Hardness (Shore A)	65	72	85	60
Tensile Strength (PSI)	815	735	1060	1100
Ultimate Elongation (%)	500	600	900	450
Tear Strength (lbs./in.)	130	165	220	130
Resistivity, at 75°F				
Volume (ohm-cm)	1.5×10^{11}	6.0×10^{11}	9.6×10^{11}	9.0×10^{11}
Surface (ohms)	2.7×10^{12}	1.4×10^{12}	2.6×10^{13}	2.3×10^{13}
Elastomer Color,	Medium amber	Light amber	Very dark	Medium amber
Clarity	Clear	Clear	Opaque	Clear

*A 7.1% available isocyanate polymer (91 poise viscosity). Products Research and Chemical Corporation.

Only TDI terminated polyethers had been studied so far in the program. At this point, other types of isocyanate terminated polyethers such as MDI (diphenylmethane diisocyanate) were investigated in order to determine if improvements in physical properties could be achieved. Urethane elastomers derived from MDI generally afford higher tear and tensile strengths, equal or slightly lower elongations, and have improved hydrolytic stability over equivalent TDI/polyether systems. The overall electrical properties are equivalent or slightly better than TDI analogues.

Two urethane polymers based on MDI and PTMG from Uniroyal Chemical were evaluated with the three diamine containing curing agents. This was a practical approach as long as the FeAA catalyst level within the curing agent was the only item requiring adjustment.

The results of the study are summarized in Table VIII. We assumed, that because the 2500 poise application lives of the TDI/PTMG and PPG based polymers all exceeded 6 hours, shorter, but acceptable worklives would be obtained with the MDI polymers of similar available isocyanate content. This proved not to be the case. The time to reach a mixed viscosity of 2500 poise ranged between 12 and 90 minutes, even when the FeAA catalyst was reduced to 15% of its initial concentration. Performance properties could not be determined for the Cyanacure system because the application life was only 12-18 minutes at 75°F.

If the FeAA catalyst was totally eliminated, unsuitable elastomers were obtained because there was now an imbalance between the hydroxyl/isocyanate and diamine/isocyanate reaction rates. This resulted in incompatibility and partial gelling during handling. The high activity level is due to the structural differences between 2,4-TDI and MDI. The rate constant for MDI at 86°F with diethylene glycol adipate is 0.34×10^4 liters/mole-second. Under similar conditions the rate constant for the isocyanate in the 2-position of TDI is 0.057×10^4 liters/mole-second and 0.45×10^4 liters/mole-second for the isocyanate in the 4 position of TDI (1). We assume that when the initial prepolymer is manufactured, the isocyanate in the 4-position of TDI is consumed first. This leaves nearly a six-fold difference in activity between the isocyanate groups of MDI and the isocyanate group in the 2-position of TDI. MDI systems will require a new curing agent to be developed for which time in this program was not available.

The use of MDI polymers becomes less attractive when one considers polymer stability. We had to request a second set of materials from the supplier as the first units were well below published specification values for both available isocyanate content and viscosity. The two MDI containing polymers showed evidence of crystallizing after 24-48 hours storage at 71-77°F. During successive recrystallizations at 120°F, these polymers tended to lose available isocyanate and increase in viscosity. Partially full containers were most difficult to handle, and had to be well purged with dry nitrogen to ensure even a semblance of shelf stability. If this was not done, the polymer formed a medium off-white, opaque insoluble material. The insoluble material, probably dimerized MDI, could not be converted into active monomer by the application of mild heat. The polymer was no longer usable at this point.

(1) Saunders, J.H. and Frisch, K.C. "Polyurethane Chemistry and Technology, Part I, Chemistry". Interscience, (1962), 129-215.

TABLE VIII
MDI/PTMG POLYMER EVALUATION*

	Polycure 1000		Cyanacure		Permapol D-562	
	VB-625	VB-635	VB-625	VB-635	VB-625	VB-635
Polymer Viscosity (poise at 75°F)	300	215	300	215	300	215
Mixed Viscosity (poise at 75°F)	255	190	--	--	250	180
Application Life, Hrs. (time to 2500 poise)	1.50	1.00	0.30	0.20	1.00	0.75
Hardness (Shore A)	65	74	--	--	65	74
Tensile Strength (PSI)	2605	3205	--	--	2565	3235
Ultimate Elongation (%)	500	350	--	--	400	380
Tear Strength (lbs./in.)	220	205	--	--	210	230
Resistivity at 75°F						
Volume (ohm-cm)	2.6×10^{10}	3.8×10^{11}	--	--	8.2×10^{10}	2.7×10^{11}
Surface (ohms)	6.2×10^{11}	9.1×10^{12}	--	--	2.8×10^{11}	3.1×10^{12}
Elastomer Color,	Med. amber	Med. amber	--	--	Med. amber	Med. amber
Clarity	Clear	Clear	--	--	Clear	Clear

*Uniroyal Chemical, VB-625, 6.36% available isocyanate.
VB-635, 7.73% available isocyanate.

TABLE IX
DIAMINE CONTAINING CURING AGENTS WITH PERMAPOL U-47*

	Polycure 1000	Cayanacure	Permapol D-562
Mixed Viscosity (poise at 75°F)	140	155	130
Application Life, Hrs. (time to 2500 poise)	2.5	1.0	2.75
Hardness (Shore A)	85	89	84
Tensile Strength (PSI)	4895	4181	4645
Ultimate Elongation (%)	470	510	480
Tear Strength (lbs./in.)	311	355	271
Elastomer Color,	Medium amber	Medium amber	Dark amber
Clarity	Clear	Clear	Clear
Resistivity, At 75°F			
Volume (ohm-cm)	$2.6x10^{11}$	$1.9x10^{12}$	$3.4x10^{11}$
Surface (ohms)	$4.0x10^{12}$	$4.3x10^{13}$	$6.2x10^{12}$
Insulation Resistance (megohms at 75°F)	$4.9x10^{4}$	$1.7x10^{5}$	$9.4x10^{4}$
Power factor at 75°F			
1 KHz	0.093	0.093	0.090
1 MHz	0.056	0.059	0.056
Dielectric Constant at 75°F			
1 KHz	5.8	5.9	5.8
1 MHz	4.2	4.2	4.2

*An 8.8% available isocyanate based upon TDI/PPG. Products Research and Chemical Corporation.

SELECTION OF FINAL CANDIDATES

The three remaining diamine cure systems were to be evaluated with Permapol U-47 and Adiprenes L-100, L-167 and L-200. The Permapol U-47 is a non-crystallizing polymer while the latter three will crystallize at temperatures below 65°F.

The point was now reached in the program where a final selection criterion was necessary prior to starting the extensive environmental testing. The basis for the final selection was determination of sound speed. These critical tests were conducted by NRL, Underwater Sound Reference Detachment in Orlando, Florida. Table X summarizes the test results.

On reviewing of the sound velocity determinations. There appears to be a direct correlation between sound speed and both cured elastomer hardness and available isocyanate content of the urethane polymer. This initial observation may be an oversimplification as the true relation is apparently quite complex. Dr. Corley Thompson of NRL has conducted a series of carefully designed experiments showing that sound velocity through a polyether urethane is inversely proportional to polymer average molecular weight. (2) For example, NRL has shown that if curing agent composition is held constant, urethane polymers prepared from various molecular weights of PTMG exhibit an inverse relation between molecular weight and sound speed when the isocyanate/hydroxyl equivalent ratio of the polymer is maintained at 2.0/1.0.

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(2) Maurice, W.T., (PRC) and Thompson, C.M., (NRL) Private communication, (August 1982).

TABLE X
SOUND SPEED AT 75°F

Curative/Polymers	Sound Speed (meters/second)	Isocyanate Content (%)	Hardness (Shore A)
Polycure 1000			
L-100	1604	4.1	67
L-167	1659	6.6	70
L-200	1718	7.5	78
U-47	1801	8.8	85
Cyanacure			
L-100	1599	--	53
L-167	1647	--	55
L-200	1714	--	65
U-47	1799	--	89
Permapol D-562			
L-100	1605	--	64
L-167	1658	--	68
L-200	1730	--	74
U-47	1819	--	84

The sound speed data of Table X was reviewed by NRL to eliminate those elastomers with unsuitably high sound velocities. The cut off velocity was 1715 meters/second. Thus, the following materials were excluded from the remainder of the program:

1. All formulations derived from Permapol U-47.
2. Formulations of Adiprene L-200 with Polycure 1000 and Permapol D-562 curing agents.

Seven potential encapsulant formulas remained for the last phase of the program. The final tests were:

1. General Handling and Performance Properties, Table XI.
2. General Electrical Properties, Table XII.
3. Physical Hydrolytic Stability, 120 Days, 158°F/99% RH, Table XIII.
4. Resistance of Electrical Properties to Wet or Humid Environments, Table XIV.
5. Stress/Strain: Resistance to 60 Day Water Immersion at 122°F, Table XV.
6. Stress/Strain: Resistance to 1000 Hours Castor Oil Immersion at 122°F, Table XVI.
7. Stress/Strain Specimen Analysis, Tables XVII, XVIII and XIX.
8. Encapsulant Raw Material Costs.
9. Low Temperature Flexibility.
10. Fungus Resistance.
11. Water Vapor Permeability.
12. Attenuation of the Acoustic Wave.

The mixing ratios, by weight, of the final candidates are shown below:

	Polycure 1000		Cyanacure			Permapol D-562	
	L-100	L-167	L-100	L-167	L-200	L-100	L-167
Curing Agent	19.0	29.6	17.8	27.3	32.5	18.8	28.8
Polymer	100.0	100.0	100.0	100.0	100.0	100.0	100.0

GENERAL HANDLING AND PERFORMANCE PROPERTIES

The general handling, mechanical and adhesion properties of the seven candidate urethane encapsulants are summarized in Table XI. The most outstanding features are the excellent compression sets, tear strengths, tensile strengths, and ultimate elongations considering that these are all medium hardness range materials.

System application lives are all long enough so that premixed and frozen packaging is feasible should the end user desire it. The initial mixed viscosities of the Adiprene L-100 systems are on the high side. Our choice from a material handling point of view would be the Vibrathane B-601 or Adiprene L-167 formulas. The much lower viscosities in this instance make premixed and frozen packaging even more desirable. The Adiprene L-200 polymers offered no real advantage over that of L-167, and as will be seen later had a marginally acceptable high sound speed. The Polycure and Permapol curing agents were essentially equivalent in overall performance, but hold a slight edge over the corresponding Cyanacure systems.

The evaluation of adhesion to various substrates was conducted using state-of-the-art surface preparation and primers as summarized below:

1. PVC
   The PVC corresponded to MIL-I-7444. The surface was tackified with clean, oil free methyl ethyl ketone. The encapsulant was then applied. Samples were prepared and tested according to MIL-M-24041C. The test results of 25 lbs/inch width of peel or more are considered excellent.

2. Neoprene
   The rubber corresponded to MIL-R-3065. The surface was mechanically abraded with a clean, grease free wire wheel. A liberal coat of PR-1523-M Primer was brush applied to the abraded neoprene surface. The excess primer was wiped off with a lint free cotton gauze pad after air drying 30-35 minutes. The encapsulant was then applied. Samples were prepared and tested as per MIL-M-24041C. The peel adhesion values are considered quite good.

3. Stainless Steel
   The metal corresponded to MIL-S-5059. The panels were cleaned with oil free methyl ethyl ketone and primed with PR-420 primer. The primer was allowed to dry 60 minutes at ambient temperature prior to encapsulating. The peel values all exceed 40 lbs/inch.

4. Transducer Ceramic
   Samples of transducer ceramic were of the PZT type which had a silver surface finish. These were supplied by NRL. The silver surface was cleaned with methyl ethyl ketone prior to application of PR-1533. This is a primer especially developed for precious metal surfaces. The primer was air dried 70 minutes at ambient temperature prior to encapsulating. The failure mode was all low level adhesive between the silver film and the ceramic surface at 5 to 6 lbs/inch. The adhesion of the encapsulant to the primed silver appeared to be excellent. We suspect the ceramic samples were not new and had been used previously. This specific test result should be repeated by NRL using new ceramic elements.

GENERAL ELECTRICAL PERFORMANCE

Electrical test data are summarized in Table XII. Volume and surface resistivities, as well as insulation resistances are a little more than one decade lower than the target profile, and between 2 and 3 decades lower in insulation resistance. As stated earlier, use of other PTMG based polymers might improve electrical properties. In support of this concept, the Permapol D-562/Adiprene L-100 system was re-examined where Uniroyal Vibrathane B-600 was used in place of the Adiprene. The respective resistivity and insulation resistances are compared below:

	Permapol D-562 Adiprene L-100	Permapol D-562 Vibrathane B-600
Volume Resistivity at 75°F, ohm-cm	2.2×10^{10}	4.7×10^{10}
Insulation Resistance at 75°F, megohms	1.20×10^{3}	8.0×10^{3}

There is a noticeable difference electrically between two ostensibly equivalent PTMG based polymers. The Vibrathane B-600 shows an insulation resistance 6.7 times higher and a volume resistivity over twice as high as the Adiprene. We would not expect to see similar large variances between dielectric constants or power factors, for in our experience, these properties have proven much more insensitive to variations in raw materials or manufacturing processes.

The values obtained for dielectric strength are somewhat lower than expected. Values in the range 300-315 volts/mil for 125 mil thick samples would be more typical. The sound velocities are all good save for the marginal Cyanacure/L-200 value of 1714 meters/second.

The dielectric constants and power factors are all somewhat higher than those normally found in liquid castable PTMG based/MBOCA urethanes tested at frequencies of 1KHz and 1MHz. They are not however, outside the range found in high performance, non-MBOCA liquid castable polyether urethanes currently available.

We believe that, except for the modest difference in electrical properties discussed above, the Vibrathane and Adiprene PTMG based polymers are equivalent and either would be suitable for the intended application. In support of this conclusion, comparative mechanical properties of cured urethane elastomers derived from the four polymers and the Polycure 1000 liquid curing agent are given below:

	Vibrathane B-600	Adiprene L-100	Vibrathane B-601	Adiprene L-167
Hardness	68 A	67 A	71 A	70 A
Modulus at				
100% extension	271 psi	266	256	235
200	372	366	377	357
300	549	531	454	471
400	779	775	739	794
500	1591	1603	1606	1677
Tensile Strength	3378 psi	3304	3394	3475
Tear Strength	185 lbs/in	188	208	185
Ultimate Elongation	630%	625	600	615

TABLE XI
GENERAL HANDLING AND PERFORMANCE DATA OF FINAL CANDIDATE ENCAPSULANTS

Curative/Polymer	L-100	L-167	L-100	L-167	L-200	L-100	L-167
	Polycure 1000		Cyanacure			Permapol D-562	
Mixed Viscosity (poise at 75°F)	300	110	380	120	115	250	70
Application Life, Hrs. (time to 2500 poise)	7	7.5	7	7	7	7	7
Hardness (Shore A)	67	70	53	55	65	64	68
Modulus (PSI) at							
100% extension	263	237	176	141	185	269	173
200% extension	364	336	238	192	264	383	234
400% extension	770	758	389	320	574	854	431
500% extension	1582	1659	560	408	1385	1817	686
Tensile Strength (PSI)	3280	3255	2899	2765	3311	2815	2585
Ultimate Elongation (%)	630	600	700	650	600	600	625
Tear Strength (lbs./in.)	178	187	93	105	150	153	143
Compression Set (22 hrs/158°F), % Set	32	20	18	12	7	21	8
Adhesion to (lbs./in. width)*							
PVC	26	26	25	28	26	26	25
Neoprene	23	23	23	24	25	23	23
Stainless Steel	43	40	41	41	44	41	40
Transducer Ceramic	6	-	-	5	-	-	5
Volume Shrinkage (% volume decrease)	3.7	3.2	3.9	4.4	4.4	3.8	3.8

TABLE XII
GENERAL ELECTRICAL PROPERTIES OF FINAL CANDIDATE ENCAPSULANTS

Curative/Polymer	Polycure 1000		Cyanacure			Permapol D-562	
	L-100	L-167	L-100	L-167	L-200	L-100	L-167
Resistivity							
Volume, ohm-cm							
at 75°F	1.7×10^{10}	3.1×10^{10}	4.7×10^{10}	1.5×10^{11}	3.8×10^{11}	2.2×10^{10}	4.8×10^{10}
at 150°F	4.3×10^{8}	5.9×10^{8}	1.1×10^{9}	8.3×10^{9}	9.7×10^{9}	5.4×10^{8}	7.3×10^{8}
Surface, ohms							
at 75°F	3.4×10^{11}	5.4×10^{11}	1.3×10^{12}	5.7×10^{12}	1.2×10^{13}	4.2×10^{11}	7.9×10^{11}
at 150°F	1.1×10^{10}	8.3×10^{9}	1.0×10^{11}	1.9×10^{11}	9.3×10^{11}	1.0×10^{10}	3.6×10^{10}
Electrical Insulation Resistance, megohms							
at 75°F	1.6×10^{3}	3.8×10^{3}	3.8×10^{3}	8.2×10^{3}	5.1×10^{4}	1.2×10^{3}	7.9×10^{3}
at 150°F	1.1×10^{3}	1.6×10^{2}	1.6×10^{2}	2.4×10^{2}	6.9×10^{2}	2.0×10^{2}	3.5×10^{3}
Power factor at 75°F							
at 1 KHz	0.094	0.088	0.068	0.080	0.097	0.106	0.090
at 1 MHz	0.092	0.075	0.088	0.074	0.056	0.089	0.069
Dielectric Constant at 75°F							
at 1 KHz	8.2	7.5	8.0	7.6	6.2	7.9	7.2
at 1 MHz	5.3	4.8	5.3	4.8	4.3	5.2	4.7
Sound Velocity at 75°F (meters/sec)*	1604	1659	1599	1647	1714	1605	1658
Dielectric Strength Volts/mil, 125 mil thick sample	270	270	290	290	300	280	280

*Test values supplied by NRL, Underwater Sound Reference Detachment.

TABLE XIII
PHYSICAL HYDROLYTIC STABILITY
(158°F/99% RH)

SYSTEM	Initial	5 days	19 days	40 days	54 days	97 days	120 days	% Loss Hardness Sample State
Polycure 1000								
Adiprene L-100								
Hardness, Shore A	66	62	60	60	58	54	51	-22.7%
% Weight Change		+2.01	+2.06	+2.07	+2.11	+2.32	+2.41	Elastomer
Adiprene L-167								
Hardness	66	57	57	57	57	53	50	-24.2%
% Weight Change		+1.76	+2.08	+2.30	+2.18	+2.37	+2.44	Elastomer
Permapol D-562								
Adiprene L-100								
Hardness	63	60	59	57	56	52	50	-20.6%
% Weight Change		+1.67	+2.04	+2.18	+1.93	+2.47	+2.38	Elastomer
Adiprene L-167								
Hardness	63	57	56	55	55	51	50	-20.6%
% Weight Change		+1.92	+2.25	+2.39	+1.96	+2.70	+2.44	Elastomer
Cyanacure								
Adiprene L-100								
Hardness	55	52	50	48	47	40	35	-36.4%
% Weight Change		+1.63	+1.98	+1.95	+1.78	+1.99	+2.06	Elastomer
Adiprene L-167								
Hardness	54	46	45	45	44	35	32	-40.7%
% Weight Change		+1.66	+2.08	+2.10	+1.96	+2.15	+2.21	Elastomer
Adiprene L-200								
Hardness	64	52	48	46	45	33	30	-53.1%
% Weight Change		+1.94	+2.28	+2.33	+2.13	+2.47	+2.56	Elastomer

PHYSICAL HYDROLYTIC STABILITY

The results of the 120 day, 158°F/99% RH Hydrolytic Stability test are presented in Table XIII. All elastomer formulas exhibited about the same degree of moisture absorption. The Polycure and Permapol urethanes lost the same amount of hardness over the term of exposure. The Cyanacure systems show significant inferiority in this respect, losing between 36 and 53% of their initial hardness. The 20-22% hardness losses observed for the Polycure and Permapol urethanes are not unusual if one considers the criterion set forth in MIL-M-24021. The specification allows a 20% maximum loss in hardness after the same exposure conditions, but covers a hardness range of 70 to 92 Shore A. In actuality, those urethanes listed on the Qualified Products List of MIL-M-24041C all exceed 80 Shore A in hardness. This test has a more drastic effect in the percentage of hardness lost the lower the initial hardness of the product tested. The Polycure and Permapol based encapsulants are lower at 60-62 Shore A and those of Cyanacure even more so at 55-64 Shore A.

The bis(phenylthio)ethane structure of the Cyanacure based elastomers appears more susceptible to plasticization by moisture than do the orthoester substituted methylene bis(anthranilates) of the other curatives. The concept of moisture plasticization is defined accordingly: Water permeates the polymer matrix and cleaves the intermolecular hydrogen bonds between urethane and urea sites on adjacent polymer chains. New hydrogen bonds are now formed between water and the urea/urethane linkages of the individual polymer chains. The result of this is that both hardness and modulus are reduced. This is exactly what is found in the stress/strain data of Table XV. As long as no irreversible polymer degradation occurs, such as actual destruction of backbone urea or urethane sites, a good portion of physical property loss will be regained as the material dries out. The general hydrolytic stability of these medium hardness urethanes is nevertheless good. The fact that all encapsulants remained elastomeric is sufficient evidence that no extensive polymer chain scission took place. In addition, had irreversible chain degradation occured, it would have been reflected in the electrical performance data under wet or humid conditions of Table XIV.

CHANGES IN ELECTRICAL PROPERTIES UNDER WET OR HUMID CONDITIONS

Electrical insulation resistance and high potential resistance samples were exposed 28 days to 158°F and 99% RH. All formulas employing Adiprene L-167 performed very well. See Table XIV. The Adiprene L-100 formulas did well, but fell half a decade below that of their L-167 analogues. These results are quite acceptable and are of the same order and magnitude that we observed several years ago testing a number of Adiprene and MBOCA containing elastomers under the same conditions.

The high potential resistance after the same exposure was determined by applying 2000 VRMS and observing any current leakage. Current leakage, if any, was less than the 2.0 microamperes minimum detectable level of the test instrument.

The last electrical test conducted was volume resistivity of samples immersed 60 days in 122°F water. In all instances, the resistivity was essentially unchanged.

TABLE XIV
RESISTANCE OF ELECTRICAL PROPERTIES TO WET OR HUMID ENVIORNMENTS

HIGH POTENTIAL RESISTANCE*
(158°F/99% RH)
(leakage value in microamperes)

System	Initial	After 28 Days Exposure
Cyanacure		
Adiprene L-100	0	0
Adiprene L-167	0	0
Adiprene L-200	0	0
Polycure		
Adiprene L-100	0	0
Adiprene L-167	0	0
Permapol D-562		
Adiprene L-100	0	0
Adiprene L-167	0	0

*Electrical measurements determined after samples stabilized 2 hours at 75°F, 50± 5.0% RH. Samples prepared and tested as per MIL-M-24041C, Paragraphs 4.7.4.5 and 4.7.4.6. Applied voltage is 2000 VRMS using a Slaughter High Potential Leakage Tester Model 22/125-2.5. Minimum detectable leakage rate of 2 microamperes.

Volume Resistivity
Direct water Immersion at 122°F (50°C)
(values in ohm-cm at 75°F)

System	Initial	7 Days	29 Days	60 Days Exposure*
Polycure 1000				
Adiprene L-100	2.1×10^{10}	2.8×10^{10}	2.9×10^{10}	1.4×10^{10}
Adiprene L-167	3.5×10^{10}	7.5×10^{10}	8.1×10^{10}	2.3×10^{10}
Cyanacure				
Adiprene L-100	1.8×10^{10}	2.0×10^{10}	1.3×10^{10}	9.9×10^{9}
Adiprene L-167	6.1×10^{10}	5.2×10^{10}	4.9×10^{10}	2.1×10^{10}
Adiprene L-200	3.1×10^{11}	1.8×10^{11}	1.2×10^{11}	4.9×10^{10}
Permapol D-562				
Adiprene L-100	2.9×10^{10}	5.0×10^{10}	6.0×10^{10}	4.7×10^{10}
Adiprene L-167	5.7×10^{10}	8.9×10^{10}	1.3×10^{11}	3.2×10^{10}

*Test values obtained after sample aged 2 hours, 72-77°F / 50 ± 5.0% R.H. Samples prepared and tested as per MIL-M-24041C, paragraphs 4.6.1 and 4.7.4.4.

TABLE XIV (Continued)
RESISTANCE OF ELECTRICAL PROPERTIES TO WET OR HUMID ENVIRONMENTS
(158°F/99% RH)

ELECTRICAL INSULATION RESISTANCE* (Values in Megohms)

System	Initial	7 days	14 days	21 days	28 days
Permapol D-562					
Adiprene L-100	1.21×10^3	4.0×10^2	3.8×10^2	4.1×10^2	5.0×10^2
Adiprene L-167	7.00×10^3	1.1×10^3	1.1×10^3	1.0×10^3	1.0×10^3
Polycure 1000					
Adiprene L-100	1.55×10^3	6.0×10^2	5.0×10^2	6.5×10^2	6.5×10^2
Adiprene L-167	4.00×10^3	7.0×10^2	7.0×10^2	8.5×10^2	1.0×10^3
Cyanacure					
Adiprene L-100	3.2×10^3	3.6×10^2	3.6×10^2	4.5×10^2	4.5×10^2
Adiprene L-167	8.5×10^3	1.0×10^3	1.0×10^3	1.2×10^3	1.2×10^3
Adiprene L-200	5.6×10^4	3.3×10^3	3.0×10^3	3.6×10^3	3.2×10^3

*Electrical measurements determined after samples stablized 2 hours at 75°F/50± 5.0% RH. Samples prepared and tested as per MIL-M-24041C.

PHYSICAL RESISTANCE TO FLUID IMMERSION

The water and castor oil resistance tests were the most extensive of the entire program. Stress/strain analysis, coupled with hardness and weight change were determined.

1. Water Resistance
   The seven candidate encapsulants were immersed in 122°F distilled water for a 60 day term. Periodically, samples were withdrawn to determine hardness, modulus, tensile strength and ultimate elongation. As much statistical variation as possible was eliminated in the comparative data by using tensile samples of constant 75-85 mil thickness. At least 5 specimens were tested for each individual data point. The obvious high and low statistical outliers were eliminated from the final computation. The samples, once removed from the immersion media, were all tested within a 5-6 hour period. The results are summarized in Table XV.

We believe it would be improper to compare modulus values over the entire range of elastomer extension because the cured elastomer will not experience in service conditions of high extension. A more practical approach from a field performance point of view would be to consider modulus changes up to and including 300% extension. Under this criteria, six out of the seven urethanes shown in Table XV exhibit modulus and ultimate elongation changes below 25%. The one outlier is the Permapol D-562/Adiprene L-167 combination which we feel would fall within the 25% maximum change if the test were repeated because of similarites in overall chemical structure to the other systems.

TABLE XV
RESISTANCE TO 60 DAY WATER IMMERSION AT 122°F (50°C)

Polycure 1000

Adiprene L-100	Initial	7 Days	14 Days	21 Days	29 Days	42 Days	60 Days	% Change (Initial/Final)
Hardness	67 A	68 A	68 A	64 A	64 A	64 A	62 A	-7.5
Modulus at								
100% extension	263 psi	263 psi	260 psi	261 psi	256 psi	263 psi	255 psi	-3.0
200%	364	383	348	356	346	363	349	-4.1
300%	515	524	476	492	466	495	475	-7.8
400%	770	809	705	753	663	757	704	-8.6
500%	1582	1570	1321	1465	1178	1465	1308	-17.3
540%	2567	--	--	--	--	--	--	
550%	--	2501	2260	2265	1874	2575	2121	
560%	2800*	2886	2654	--	--	--	--	
570%		--	--	--	--	3248*	--	
580%		2980	3173	--	--		2671*	
590%		--	3800*	--	--			
600%		3307*		3156*	3455*			

Adiprene L-167	Initial	7 Days	14 Days	21 Days	29 Days	42 Days	60 Days	% Change (Initial/Final)
Hardness	70 A	66 A	66 A	64 A	62 A	61 A	62 A	-11.4
Modulus at								
100% extension	237	215	207	--	215	237	230	-3.0
200%	336	311	295	--	318	349	317	-5.7
300%	466	433	440	--	459	520	430	-7.7
400%	758	664	689	--	743	810	610	-19.5
450%	--	--	--	--	1011	--	--	--
500%	1659	1210	1511	-	1805*	2217	1020	-38.5
510%	--	--	--	--		2486*	--	
520%	--	--	1754*	--			--	
540%	2636	2209		--			--	
550%	--	--		--			1453	
560%	2938*	--		--			2091*	
600%		2407*		--				

* Ultimate elongation.

TABLE XV (Continued)
RESISTANCE TO 60 DAY WATER IMMERSION AT 122°F (50°C)

Permapol D-562

Adiprene L-100	Initial	7 Days	14 Days	21 Days	29 Days	42 Days	60 Days	% Change (Initial/Final)
Hardness	68 A	68 A	68 A	65 A	65 A	64 A	65 A	-4.4
Modulus at								
100% extension	269 psi	274 psi	277 psi	281 psi	227 psi	244 psi	219 psi	-18.6
200%	383	3[illegible]	382	391	306	329	299	-21.9
300%	534	564	553	587	420	445	418	-21.7
400%	854	985	876	965	637	680	605	-29.6
450%	--	--	--	1535	--	--	--	--
500%	1817	2349	2258	2958*	1348	1432	1138	-37.4
520%	--	3328*	3100*		--	--	--	--
550%	3742*				2333	2872	1879	-49.8
560%					--	3265*	--	
570%					2928*	--	--	
580%							2874*	

Adiprene L-167	Initial	7 Days	14 Days	21 Days	29 Days	42 Days	60 Days	% Change (Initial/Final)
Hardness	63 A	61 A	60 A	58 A	58 A	57 A	57 A	-9.5
Modulus at								
100% extensior	173	210	208	211	208	206	217	+25.4
200%	234	304	290	315	290	292	320	+36.8
300%	314	454	438	433	440	440	481	-53.2
400%	431	756	811	695	778	755	872	+102.3
450%	--	--	--	--	1683	--	1394	--
500%	686	2099	2749*	1871	2572*	2226	2570*	+274.0
510%	--	--		--		2504*		
520%	--	2513*		2332*				
600%	1621							
650%	2293*							

* Ultimate elongation.

TABLE XV (Continued)
RESISTANCE TO 60 DAY WATER IMMERSION AT 122°F (50°C)

Cyanacure	Initial	7 Days	14 Days	21 Days	29 Days	42 Days	60 Days	% Change (Initial/Final)
Adiprene L-100								
Hardness	55 A	55 A	55 A	53 A	52 A	51 A	50 A	9.1
Modulus at								
100% extension	176 psi	163 psi	155 psi	158 psi	158 psi	155 psi	153 psi	-13.1
200%	238	216	207	209	214	209	203	-14.7
300%	303	267	265	265	270	263	253	-16.5
400%	389	369	348	357	365	344	318	-18.3
500%	560	549	521	511	571	498	451	-19.5
600%	1295	1436	1454	1554	1546	1236	939	-27.5
620%	2120	--	2180	2173*	2321*	--	--	
640%	--	2691*	2190*			2693*	--	
650%	--						1994	
670%	--						2443*	
700%	2899*							
Adiprene L-167								
Hardness	60 A	57 A	57 A	55 A	54 A	53 A	52 A	-13.3
Modulus at								
100% extension	141	204	200	218	152	145	171	+21.3
200%	192	284	270	317	216	195	224	+16.7
300%	241	381	380	463	288	260	285	+18.3
400%	320	639	592	762	405	354	388	+21.3
500%	408	989	1453	1700*	664	533	592	+45.1
530%	--	--	1878*		--	--	--	--
550%	--	1659			988	736	864	--
580%	--	1984*			--	--	--	--
600%	788				1830	1204	1440	+82.7
620%	--				2285*	1898*	--	
625%	--						2470*	
680%	2765*							

*Ultimate elongation.

TABLE XV (Continued)
RESISTANCE TO 60 DAY WATER IMMERSION AT 122°F (50°C)

Cyanacure

Adiprene L-200	Initial	7 Days	14 Days	29 Days	42 Days	60 Days	% Change (Initial/Final)
Hardness	62 A	60 A	57 A	54 A	53 A	52 A	-16.1
Modulus at							
100% extension	185 psi	205 psi	198 psi	192 psi	170 psi	181 psi	-2.2
200%	264	296	272	254	243	247	-6.4
300%	371	587	377	355	338	329	-11.3
400%	574	745	547	561	525	479	-16.6
500%	1385	1959*	1315	1299	1260	909	-34.4
530%	--		2232*	--	--	--	--
550%	2715			2522*	2488	1782	-34.4
560%	--				2742*	--	
570%	--					2341*	
600%	3311*						

*Ultimate elongation.

The basic difference between the Polycure/Permapol systems and Cyanacures is the apparent higher hydrophobicity of the former two. This conclusion is supported by the relative changes in hardness we observed during the 120 day, 158°F/99% RH exposure in which the three Cyanacure urethanes all remained elastomers, but lost a far higher percentage of their initial hardness.

2. Castor Oil Resistance

The results of the 1000 hour, 122°F castor oil immersions are summarized in Table XVI. The effect of castor oil immersion on moduli changes was greater than that observed with water. We selected the TDI/PTMG based polymers for study as they offered the best chance for castor oil resistance over urethane polymers derived from polyoxypropylene glycol (PPG) or hydroxy terminated polybutadiene (HPBD). We observed losses in ultimate elongations ranging from 9 to 46%. Of the seven formulas tested, all exhibited moduli increases over the 100 to 300% extension range. The concept of modulus increase is defined here to mean that the actual modulus change at any given extension went from a negative value to either a smaller negative value or a positive number as the material was extended from 100 up to 300%. This suggests that while castor oil immersion tended to reduce modulus at any given extension over time, the adverse effect on that modulus change became less pronounced at higher extensions.

The Polycure 1000/Adiprene L-100 and L-167, Permapol D-562/Adiprene L-100 and Cyanacure/Adiprene L-167 systems all meet our criterion of less than 25% moduli change. The Cyanacure/Adiprene L-100 and L-200 formulas gave the highest absolute moduli changes.

TABLE XVI
RESISTANCE TO 1000 HOURS CASTOR OIL IMMERSION AT 122°F (50°C)

Polycure 1000

Adiprene L-100	Initial	7 Days	14 Days	21 Days	29 Days	42 Days	% Change (Initial/Final)
Hardness	67 A	67 A	64 A	62 A	59 A	59 A	-11.90
Modulus at							
100% extension	263 psi	250 psi	254 psi	238 psi	199 psi	226 psi	-14.10
200%	364	371	372	356	309	367	+0.82
300%	515	559	543	547	460	589	+14.40
350%	--	--	--	--	--	772	--
400%	770	845	940	983	804	1164*	+51.20
450%	--	1396*	1381	1150*	1119		
460%	--		--		1265*		
480%	--		1829*				
500%	1582						
540%	2567						
560%	2800*						
Adiprene L-167							
Hardness	70 A	65 A	62 A	58 A	58 A	57 A	-18.60
Modulus at							
100% extension	237	194	197	--	179	179	-24.50
200%	336	290	299	--	283	290	-13.70
300%	466	422	447	--	413	426	-8.60
400%	758	647	702	--	671	735	-3.00
450%	--	--	1200	--	--	--	--
460%	--	--	1292*	--	--	--	--
500%	1659	1206		--	1299*	1538	-7.30
510%	--	--		--	--	1843*	
550%	--	1919*		--	2098*		
560%	2938*						

*Ultimate elongation.

TABLE XVI (Continued)

RESISTANCE TO 1000 HOURS CASTOR OIL IMMERSION AT 122°F (50°C)

Permapol D-562

Adiprene L-100	Initial	7 Days	14 Days	21 Days	29 Days	42 Days	% Change (Initial/Final)
Hardness	68 A	63 A	60 A		58 A	58 A	-14.7
Modulus at							
100% extension	269 psi	254 psi	250 psi	231 psi	211 psi	241 psi	-10.7
200%	383	390	370	347	317	402	+4.9
300%	534	567	579	550	402	586	+9.7
350%	--	--	--	--	667	867*	--
400%	854	926	1036	902	938*		+9.8
450%	--	1379*	1267*	1173*			
500%	1817						
550%	3742*						

Adiprene L-167	Initial	7 Days	14 Days	21 Days	29 Days	42 Days	% Change (Initial/Final)
Hardness	63 A	60 A	55 A	54 A	50 A	50 A	-20.6
Modulus at							
100% extension	173	175	176	167	174	177	+2.3
200%	234	270	274	273	279	295	+26.1
300%	314	415	436	415	464	490	+56.1
350%	--	--	--	--	615	767*	
400%	431	671	848	736	821*		
450%	--	927	1131	1155*			
480%	--	1093*	1587*				
500%	686						
600%	1621						
650%	2293*						

*Ultimate elongation.

TABLE XVI (Continued)
RESISTANCE TO 1000 HOUR CASTOR OIL IMMERSION AT 122°F (50°C)

Cyanacure

Adiprene L-100	Initial	7 Days	14 Days	21 Days	29 Days	42 Days	% Change (Initial/Final)
Hardness	55 A	55 A	--	--	40 A	40 A	-27.3
Modulus at							
100% extension	176 psi	121 psi	120 psi	98 psi	90 psi	73 psi	-58.5
200%	283	177	166	151	138	120	-57.6
300%	303	221	242	228	218	185	-38.9
400%	389	317	330	333	339	283	-27.2
450%	--	--	--	--	495	--	
500%	560	413	574	627	1353*	559	0.0
550%	--	--	--	1262*		1663*	
570%	--	--	1343*				
600%	1295	1048					
640%	--	1470*					
700%	2899*						
Adiprene L-167							
Hardness	60 A	51 A	48 A	45 A	44 A	41 A	-31.7
Modulus at							
100% extension	141	221	207	203	110	110	-22.0
200%	192	323	319	318	183	180	-6.3
300%	241	514	508	465	261	280	+16.2
375%	--	--	--	743*	--	--	--
400%	320	842	980		419	451	+40.9
450%	--	1306	1415*		--	--	--
470%	--	1422*			--	--	--
500%	408				928	1149	+181.6
520%	--				--	1687*	
530%	--				1350*		
600%	788						
680%	2765*						

*Ultimate elongation.

TABLE XVI (Continued)
RESISTANCE TO 1000 HOUR CASTOR OIL IMMERSION AT 122°F (50°C)

Cyanacure Adiprene L-200	Initial	7 Days	14 Days	29 Days	42 Days	% Change (Initial/Final)
Hardness	62 A	60 A	57 A	52 A	50 A	-19.4
Modulus at 100% extension	185 psi	155 psi	155 psi	129 psi	117 psi	-36.8
200%	264	223	224	191	158	-40.2
300%	371	331	324	280	288	-22.4
400%	574	503	485	462	497	-13.4
500%	1385	1050	1047	1073	1650	-19.1
510%	--	--	--	--	1845*	
530%	--	--	1735*	1840*		
550%	--	2125*				
600%	3311*					

*Ultimate elongation.

Our data shows that the castor oil resistance of the diamine curatives used with PTMG polymers decreases in the order:

Polycure 1000 > Permapol D-562 > Cyanacure

The fluid immersion studies were a very important aspect of the program. We have always believed that exposures of this nature should be conducted using sheets of cured elastomer from which tensile dumbbell specimens are freshly cut as required and dimensioned just prior to actual tensile-elongation determination. The rationale behind this philosophy is that either the aqueous or organic fluid exposure non-uniformally deforms the precut specimen thus making accurate measurement of sample crossection and thickness very difficult. This expected irregularity in samples would also increase the probability of higher than normal statistical variances in the raw test data.

The fluid immersions were conducted using all freshly cut tensile specimens in which each sample dimension was determined just prior to tensile testing. A smaller substudy was run in which the samples were precut. The necessary dimensions were determined in two ways: Using initial dimensions before immersion, and dimensions after immersion.

Tables XVII and XVIII summarize water and oil immersion data using precut tensile specimens dimensioned two ways. Only Polycure and Cyanacure curing agents were used with Adiprene L-100. The general agreement between these two approaches was surprisingly good. Comparative final elongations and tensile strengths are shown below.

	Polycure/L-100		Cyanacure/L-100	
Water Immersion	Fresh Cut	Precut	Fresh Cut	Precut
Tensile, psi	2671*	2355* (2369)**	2443*	2018 (2025)**
Ultimate Elongation, %	580	625	670	650
Castor Oil Immersion				
Tensile, psi	1164	1310 (1693)	1663	1244 (1659)
Ultimate Elongation, %	400	500	550	550

*Calculated using pretest dimensions.
**Calculated using after exposure dimensions.

TABLE XVII
RESISTANCE TO 60 DAY WATER IMMERSION AT 122°F (50°C)

(Precut Tensile Samples)

Adiprene L-100 Polycure 1000	Initial	14 Days		29 Days		60 Days		% Change (Initial/Final)	
Modulus at									
100% extension (psi)	263	252[1]	(260)[2]	206	(215)	236	(239)	-10.2	(- 9.1)
200%	364	340	(352)	295	(309)	318	(322)	-12.6	(-11.5)
300%	515	458	(474)	406	(426)	428	(433)	-16.9	(-15.9)
400%	770	647	(670)	602	(632)	606	(613)	-21.3	(-20.4)
500%	1582	1004	(1039)	984	(1030)	987	(997)	-37.6	(-37.2)
550%	---	1472	(1539)	1531	(1603)	1385	---		
560%	2800[3]	---	---	---	---	---	---		
600%		2468[3]	(2571)	2256	(2358)	1983	(2148)		
620%				2911[3]	(3042)	---	---		
625%						2355[3]	(2369)		
Cyanacure									
Modulus at									
100% extension	176	160[1]	(169)[2]	136	(142)	152	(158)	-13.6	(-10.2)
200%	238	210	(223)	194	(202)	201	(209)	-15.5	(-12.2)
300%	303	280	(297)	254	(264)	250	(259)	-17.5	(-14.5)
400%	389	376	(399)	335	(348)	321	(333)	-17.5	(-14.4)
500%	560	576	(610)	513	(533)	450	(467)	-19.6	(-16.6)
600%	1295	1738	(1840)	1260	(1310)	1016	(1060)	-21.5	(-18.1)
620%	---	2079[3]	(2532)	---	---	---	---		
650%	---			1898[3]	(1965)	2018[3]	(2025)		
700%	2899[3]								

[1] Sample dimensions determined after test exposure.
[2] Sample dimensions determined prior to test exposure.
[3] Ultimate elongation.

TABLE XVIII
RESISTANCE TO 1000 HOURS CASTOR OIL IMMERSION AT 122°F (50°C)

(Precut Tensile Samples)

Adiprene L-100

Polycure 1000	Initial	21 Days	42 Days	% Change (Initial/Final)
Modulus at 100% extension (psi)	263	194[1] (216)[2]	176 (233)	-33.1 (-11.4)
200%	364	326 (364)	282 (373)	-22.5 (+ 2.5)
300%	515	475 (526)	418 (546)	-18.8 (+ 6.0)
400%	770	892 (965)	713 (947)	-7.4 (+23.0)
450%	--	1480[3] (1577)	--	
500%	1582		1310[3] (1693)	
560%	2800[3]			

Cyanacure

	Initial	21 Days	42 Days	% Change (Initial/Final)
Modulus at 100% extension	176	109[1] (124)[2]	76 (98)	-56.8 (-44.3)
200%	238	163 (185)	126 (162)	-47.1 (-31.9)
300%	303	240 (272)	195 (251)	-35.6 (-17.2)
400%	389	368 (415)	313 (403)	-19.5 (+ 3.6)
500%	560	654 (742)	668 (857)	+19.3 (+53.0)
550%	--	--	1244[3] (1659)	
600%	1295	1327[3] (1557)		
650%	--			
700%	2899[3]			

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[1] Sample dimensions determined after test exposure.
[2] Sample dimensions determined prior to test exposure.
[3] Ultimate elongation.

TABLE XIX
COMPARATIVE TEST DATA PRECUT VERSUS FRESH CUT TENSILE SPECIMENS

	% Change Between Initial and Final Values			Standard Deviation of Moduli Data		
	Fresh Cut	Precut		Fresh Cut	Precut	
Polycure 1000/Adiprene						
60 Day Water Immersion						
Modulus at						
100% extension (psi)	-3.0[1]	-10.2[1]	(- 9.1)[2]	6.3	12.3[1]	(10.0)[2]
200%	-4.1	-12.6	(-11.5)	7.6	8.0	(4.7)
300%	-7.8	-16.9	(-15.9)	15.7	6.9	(6.9)
400%	-8.6	-21.3	(-20.4)	31.2	29.8	(23.5)
500%	-17.3	-37.6	(-37.2)	105.5	71.9	(59.3)
1000 Hour Castor Oil Immersion						
Modulus at						
100% extension	-14.10	-33.1	(-11.4)	7.1	79.6	(35.6)
200%	+ 0.82	-22.5	(+ 2.5)	21.3	42.1	(65.1)
300%	+14.40	-18.8	(+ 6.0)	47.9	21.4	(40.7)
400%	+51.20	-7.4	(+23.0)	75.0	46.1	(42.3)
Cyanacure/Adiprene L-100						
60 Day Water Immersion						
Modulus at						
100% extension	-13.1[1]	-13.6[1]	(-10.2)[2]	3.0	4.3[1]	(5.9)[2]
200%	-14.7	-15.5	(-12.2)	4.0	7.0	(5.0)
300%	-16.5	-17.5	(-14.5)	4.8	10.6	(12.3)
400%	-18.3	-17.5	(-14.4)	11.8	10.5	(15.3)
500%	-19.5	-19.6	(-16.6)	23.4	22.3	(30.7)
600%	-27.5	-21.5	(-18.1)	167.4	93.6	(80.0)
1000 Hour Castor Oil Immersion						
Modulus at						
100% extension	-58.5	-56.8	(-44.3)	6.8	4.0	(2.2)
200%	-57.6	-47.1	(-31.9)	4.6	8.0	(10.4)
300%	-38.9	-35.6	(-17.2)	11.0	19.1	(23.5)
400%	-27.2	-19.5	(+ 3.6)	30.4	37.3	(45.9)
500%	0.0	+19.3	(+53.0)	101.7	143.5	(169.7)

[1] Sample dimensions determined after test exposure.
[2] Sample dimensions determined prior to test exposure.

The freshly cut specimens which were measured after fluid exposure, but before tensile testing tended to give higher moduli values. We believe that this approach better reflects potential service conditions than using precut and premeasured test samples. Table XIX carries the analysis a step further by showing percentage changes between initial and final moduli as well as standard divation of individual modulus data points under the three sample criteria. The data supports our proposal that specimens should not be precut.

FUNGUS RESISTANCE

The three of the candidate encapsulants were selected for resistance to fungus attack as per Mil-E-5272. Adiprene L-167 cured with Polycure, Permapol and Cyanacure was totally resistant to fungus attack. No growth whatsoever was observed. The test was conducted by Truesdail Laboratories for Los Angeles, an approved non-government test facility.

ACOUSTICAL ATTENUATION

NRL will determine sound attenuation of samples already submitted for sound velocity testing.

WATER VAPOR PERMEABILITY

Cured samples of the seven candidate encapsulants have been submitted to NRL for evaluation.

SONAR ENCAPSULANT COSTS

One of the program requirements specified by NRL was to develop expected costs of the potential encapsulant. We are reporting raw material costs (RMC) for the candidates. The component prices were quoted as of September 1982. It is not possible to supply actual encapsulant total costs, because manufacturing costs differ widely between firms, and chemical companies do not usually release their manufacturing costs.

The three curing agents range in RMC between \$1.58 to \$2.09/lb. The curing agents comprise 15 to 25 weight percent of the total encapsulant. The encapsulants themselves would cost between \$2.41/lb and \$2.55/lb RMC or \$5.31 to \$5.62/Kg.

CONCLUSIONS

1. Two of the commercially available aromatic diamines referred to as potentially non-carcinogenic substitutes for MBOCA are acceptable in liquid castable urethanes. The two most common drawbacks encountered were very limited solubility in liquid urethane curing agents and poor compatibility in the cured elastomer.

2. Polycure 1000, Permapol D-562 and Cyanacure were the best general diamine curatives within the constraints of the program. The first two are the most attractive.

3. Adiprene L-167 or Vibrathane B-601 are the polymers of choice for best castor oil resistance even though both crystallize at 65°F or below.

4. Of the systems investigated, the Polycure 1000 or Permapol D-562 containing curing agent and Adiprene L-167 afforded the best combined castor oil and water resistance.

5. General encapsulant electrical properties are somewhat lower than some commercial two part castable urethanes, but may be adequate for the intended application. Vibrathane TDI/PTMG urethane polymers may give slightly better values.

6. Candidate encapsulant raw material costs run between $2.41-2.55/lb or $5.31-5.62/kg.

7. The polyurethane sonar encapsulants developed during this program are designed for a very specific end use: The encapsulation of sonar devices which employ castor oil as a fill fluid. These materials provide a level of castor oil resistance above that of commercially available polyurethane sonar encapsulants. A large portion of the sonar transducers in use today are not of the castor oil fill type. These units have been manufactured using high performance polyurethanes based upon polymers derived from polyoxypropylene glycol or hydroxy terminated polybutadiene. They have performed very well in service. Excluding marginal castor oil resistance, the latter two types of urethanes exhibit handling and performance advantages over the PTMG based systems such as noncrystallizing polymers and curing agents as well as excellent acoustical and electrical properties.

FUTURE WORK

New and unique raw materials will be required to obtain any significant improvement in castor oil resistance over today's commercially available polyurethane electrical encapsulating compounds. Towards the end of this program, Products Research & Chemical Corporation developed a series of fuel and oil resistant polyols. Preliminary studies of urethane elastomers derived from these materials show much improved thermal and oil resistance over present day state-of-the-art polyether urethanes.

A program designed to investigate the basic handling, mechanical, fluid immersion, electrical and acoustical properties of these new urethanes could well provide a generation of oil resistant sonar encapsulants.

APPENDIX

Many of the raw materials used in this program carry a tradename or trademark which is registered with the United States Patent Office. These items are listed below:

1. ADIPRENE:
   E. I. du Pont de Nemours & Company, Elastomer Chemical Department
2. APOCURE:
   M & T Chemicals Incorporated
3. BAYTEC:
   Mobay Chemical Company, Polyurethane Division
4. CYANACURE:
   American Cyanamid Company, Elastomers Department
5. DB OIL:
   Caschem Company
6. ISONOL:
   The Upjohn Company, Polymer Chemicals Division
7. POLACURE:
   Polaroid Corporation, Chemical Commercial Development Department
8. POLYCURE:
   PTM&W Industries Incorporated
9. PERMAPOL:
   Products Research & Chemical Corporation
10. VIBRATHANE:
    Uniroyal Chemical Company