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**PROPERTIES OF ADIPRENE L-100/MOCA
AS A ROOM-TEMPERATURE-CURED ADHESIVE
AND POSSIBLE SUBSTITUTES FOR IT**

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PROPERTIES OF ADIPRENE L-100/MOCA
AS A ROOM-TEMPERATURE-CURED ADHESIVE
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INTRODUCTION

Adiprene L-100/MOCA has been used as a room-temperature-cured adhesive in nuclear weapons and devices because (1) it cures at room temperature in a reasonable period of time without releasing solvents or volatile fragments, (2) it is compatible with HE and with LiH and similar salts, (3) it gives a good bond strength and will bond to most clean surfaces without a primer, and (4) it has a relatively low modulus that allows for some gap changes due to different coefficients of thermal expansion of the substrates. Recent restrictions on its use by OSHA (Occupational Safety and Health Act) make it desirable to review the properties of the material and to look for permissible substitutes.

This report reviews the pertinent properties of Adiprene L-100/MOCA and suggests some possible substitutes for it. Possible substitutes include Adiprene LW-520 cured with MDA, Conap's Conathane EN-5 and EN-7, CPR's Castethane 2124, polyol-cured Adiprene L-167 and L-315, some polyamide-cured epoxies, and some silicones.*

PROPERTIES OF ROOM-TEMPERATURE-CURED
ADIPRENE L-100/MOCA

1. Bulk Tensile Properties

Table 1 gives data on room-temperature-cured Adiprene L-100/MOCA at various temperatures and strain rates.

2. Hardness

90A, 43D (Shore).

3. Dimensional Stability

Acceptable for weapons; needs further definition when considering substitutes.

4. Compatibility

Acceptable.

*Reference to a company or product name does not imply approval or recommendation of the product by the University of California or the U.S. Atomic Energy Commission to the exclusion of others that may be suitable.

Table 1. Ring tensile data for room-temperature-cured Adiprene L-100/MOCA (12.7 phr MOCA).

Test conditions		Initial tensile modulus,	Initial shear modulus,	Midrange tensile modulus,	Midrange shear modulus,	Nominal breaking stress	Nominal breaking strain	True breaking stress
Temperature (°C)	Cross-head speed (cm/min)	E_I (kgf/cm ²)	G_I (kgf/cm ²)	E_M (kgf/cm ²)	G_M (kgf/cm ²)	(kgf/cm ²)		(kgf/cm ²)
-40	2	1933	723	412	109	828	2.76	2990
-11	0.5	403	157	184	43.8	785	3.29	3364
-11	2	458	153	205	51.5	767	3.19	3201
-11	10	861	296	223	54.4	829	3.25	3520
23	0.1	324	96	77	6.5	579	4.63	3228
23	0.5	347	116	87	8.5	718	4.46	3909
23	2	403	133	95	10.7	619	4.23	3222
23	10	436	143	112	15.8	584	4.08	2954
23	50	603	203	133	22.2	490	4.06	2466
57	0.5	261	87	62	4.5	218	4.07	1128
57	2	268	89	60.5	2.1	444	4.75	2542
57	10	361	121	62.7	3.3	331	4.71	1883
100	2	264	89	48	4.4	149	3.77	711

5. Glass Transition

-50°C ± 5°. Some higher transitions have been reported. However, it has maintained good adhesive properties in cryogenic applications at temperatures as low as 4.2°K; most LLL work was done at about 20°K.

6. Permeability

$$H_2O = 1.2-1.5 \times 10^{-9} \text{ (g-cm)/(sec-cm}^2\text{-cm Hg)}$$

$$H_2O = 0.35-12.5 \times 10^{-7} \text{ (cm}^3\text{STP-cm)/(sec-cm}^2\text{-cm Hg)}$$

$$CO_2 = 1.4-4 \times 10^{-9} \text{ (cm}^3\text{STP-cm)/(sec-cm}^2\text{-cm Hg)}$$

$$H_2 = 2.6-94 \times 10^{-6} \text{ (cm}^3\text{STP-cm)/(sec-cm}^2\text{-cm Hg)}$$

No data on He, N₂O, and NO.

7. Exotherm

Adiprene L-100/MOCA reacts exothermically. When cured at 100°C in an insulated calorimeter, the temperature of the mass rises about 20°C. Actual temperature is a function of the mass and the heat capacity of the substrate (see Fig. 1).

8. Shrinkage

About 0.5 to 0.7% when cured at room temperature; about 1.0% when mixed and cured at 100°C.

Fig. 1. Effect of exotherm on mass temperature (500-g batch; temperature of mass in insulated calorimeter). Compound: 100 parts Adiprene L-100, 12.5 parts MOCA. Polymer temperature: 212°F (100°C); MOCA temperature: 250°F (121°C).

9. Viscosity

L-100 = $18,000 \pm 3,000$ cP at 30°C.

L-167 = 4700-6500 cP at 30°C.

10. Working Time

From 15 to 30 min at ambient temperatures.

11. Cure Time

Adiprene L-100/MOCA cures slowly at room temperature. After 48 hr, it has developed about 5% of its ultimate bulk tensile strength. The 100% modulus (stress at 100% strain) is about 50% of the ultimate value after 48 hr cure. See Fig. 2. The lap-shear data from Y-12 are consistent with our cure data (Fig. 3). Butt-tensile data (Fig. 4) are somewhat higher: at 24 hr, a butt tensile strength of 1150 psi was found (80.9 kgf/cm^2). However, the butt tensile strength at 7 days was only 2150 psi (151 kgf/cm^2), considerably lower than the bulk tensile strength of the polymer.

Full cure is developed in 90 to 180 days as measured by solvent swelling.¹ The properties listed in Table 1 were determined on specimens that had aged for at least 6 months at 23°C.

12. Shelf Life

At least 1 year after manufacturing.

13. Mixing

We studied the Adiprene L-100/MOCA ratios from 11 to 14 phr of MOCA (80 to 105% of stoichiometric). Modulus decreases with increasing MOCA content, but the changes are minor. The bands in Fig. 5 show the ranges of values found with this range of MOCA. Breaking stress (Fig. 6) appears to be at a maximum at about 13 phr.

14. Vendors

Adiprene L-100/MOCA is made only by du Pont, although others repackage the material.

15. Chemistry

The components are well characterized. L-100 is a TDI-terminated polyoxybutylene glycol; the molecular weight of the prepolymer is about 2000. MOCA is essentially pure 4,4'-methylene bis(2-chloroaniline).

¹E. S. Jessop, A. T. Buckner, J. K. Lepper, and H. G. Hammon, Mixing Procedure for Adiprene L-100 and MOCA, Lawrence Livermore Laboratory, Rept. UCID-16117 (1972).

Fig. 2. Effect of cure time (at 23°C) on breaking strength of Adiprene L-100/MOCA.

Fig. 3. Lap shear strength of room-temperature-cured Adiprene L-100/MOCA (Y-12 data).

Fig. 4. Cure rate and hardness versus time for Adiprene L-100/MOCA (88.5/11.5). Circled numbers indicate the coefficient of variation for each of the four butt-tensile-strength points.

Fig. 5. Initial Young's modulus and shear modulus versus temperature for room-temperature-cured Adiprene L-100/MOCA (strain rate = $2.83 \times 10^{-2} \text{ sec}^{-1}$). In each band, the upper curve represents a MOCA content of 11 phr and the lower curve a content of 14 phr.

Fig. 6. Nominal breaking stress versus MOCA content for Adiprene L-100/MOCA (tested at 10 cm/min).

16. Toxicity

The toxicities of both L-100 and MOCA are relatively low. MOCA has been found to cause cancer in rats when fed in large amounts, but has not caused cancer in man or other animals.

17. Outgassing

A sample cured for 30 days at room temperature showed a total of 1% weight loss under high vacuum.

18. Water Content

Like all polar materials, Adiprene L-100 will absorb water when exposed to atmospheric moisture. The anhydrous polymer will equilibrate with about 0.6% H₂O at 50% RH and nearly 2% at 100% RH.

19. Extractables

This is highly dependent upon the nature of the solvent, time, and temperature. Aliphatic hydrocarbons have little effect. Aromatic hydrocarbons and polar solvents cause moderate to severe swelling. See Table 2.

Table 2. Oil, solvent, and chemical resistance of Adiprene L-100/MOCA (11 phr MOCA).^a

		Volume increase (%)			Volume increase (%)
70 hr at 212°F (100°C)			Amyl acetate		130
ASTM Oil No. 1		1	Cellosolve acetate		74
ASTM Oil No. 3		16	Cottonseed oil		4
			Amyl alcohol		6
1 week at 158°F (70°C)			Dimethyl formamide		Dissolved
ASTM Oil No. 1		1			
ASTM Oil No. 3		14	1 week at 122°F (50°C)		
Toluene		04	Ref. Fuel B		32
Diethyl phthalate		22	Denatured alcohol, 2B		56
Arochlor 1254		60	Trichloroethylene		209
Castor oil		9	Perchloroethylene		63
Ethylene glycol		5	Methyl ethyl ketone, dry		115
Triethyl phosphate		60	Methyl ethyl ketone, wet ^b		225
Automatic transmission fluid		8			

^aMixed at 212°F (100°C). Cured for 3 hr at 212°F (100°C). Test specimens were conditioned one week in air at 75°F (24°C), 50% RH, before testing.

^bContaining 2% water.

20. Solvent

Adiprene L-100 contains about 0.5% free toluene diisocyanate (TDI). This is consumed during cure.

21. Trace-Element Analysis

Essentially free from elements other than C, H, N, O, and Cl. Cl is not ionized.

ALTERNATIVE CURING AGENTS FOR ADIPRENE L-100

Most organic compounds with one or more active hydrogens will react with the terminal aromatic NCO groups in Adiprene L-100, although the rates vary widely. Within a group type, reactivity varies considerably depending on substituent activating or deactivating groups, steric hindrance, and the presence of catalysts; with this in mind, the order of reactivity of functional groups is about as follows: $AlNH_2 > ArNH_2 > RCH_2OH > RR'CHOH >$ amides, urethanes, substituted ureas, etc.

We need not consider chain extension by water or dibasic acids, as these materials release CO_2 on reaction with the NCO groups.

Aliphatic amines react too rapidly to be useful. Unhindered aromatic amines also react very rapidly; they are commonly used in spray applications where mixing is done in the spray nozzle and fast setup can be tolerated. Aliphatic diols, on the other hand, react so slowly that room-temperature cures are not practical unless catalysts are used. Aromatic diols form such a weak bond with NCO that it is readily reversible with mild heat.

The type of curing agent also has a pronounced effect on the properties of the urethane elastomer. Diol-cured Adiprene is much softer and weaker than MOCA-cured Adiprene. Blends of aromatic diamines generally give lower properties than a single aromatic diamine.

On the basis of the above considerations, the following materials deserve study as alternative curing agents for Adiprene:

1. Methylene dianiline (MDA), if melted and mixed with Adiprene, will react too fast, as indicated above. However, it might be used as a finely dispersed solid in a nonfugitive plasticizer or in an aliphatic diol. Initial attempts have not been encouraging. Pot life is only a few minutes. Du Pont makes a salt complex of MDA in DOP (Caytur 21).
2. Curithane 103 (Upjohn) is like MDA but has a functionality of 2.3. It would also have to be used as a dispersed solid as in (1), but might give better properties due to more true crosslinking.
3. Caytur 7 (du Pont; eutectic of m-phenylene diamine and cumene diamine) is a liquid at room temperature. It will cure Adiprene at room temperature but has

a very short pot life, 30-40 sec at 70°C. At best, we would have only a few minutes at room temperature.

4. Di(β -hydroxyethyl)aniline and similar materials might act as their own catalysts, and probably would be less likely to be incompatible with HE than alkyl aminopolyols. Softer cures would be expected than with aromatic diamines.
5. Ethylene oxide adducts of hydroquinone or resorcinol give somewhat better properties than aliphatic diols without the aromatic group. However, they need catalysts.
6. Isonol 93 (Upjohn), a proprietary triol, needs catalyst to cure at room temperature.
7. Aliphatic aminopolyols, such as Quadrol, diethanolamine, triethanolamine, etc., would be internally catalyzed, but there is a high probability of HE incompatibility.
8. Aliphatic diols and polyols, such as ethylene glycol, 1,4-butanediol, and trimethylolpropane, need catalysts to cure at room temperature, such as stannous octoate, dibutyltin dilaurate, ferric acetylacetonate, DABCO, etc.

The use of such catalysts, of course, poses questions of long-term behavior and HE compatibility.

ALTERNATIVE ADHESIVE SYSTEMS

The following adhesive materials are suggested as possible replacements for Adiprene L-100/MOCA in weapons and device applications. Table 3 lists some of the pertinent properties to the extent they are known; there are many properties to be measured in addition to HE compatibility, and long term behavior is, for the most part, unknown.

1. Adiprene LW-520/LD-2729, formerly LD-2699/LD-2729. A promising substitute for Adiprene L-100/MOCA is Adiprene LW-520 cured with methylene dianiline (MDA), distributed by du Pont as LD-2729. LW-520 has the same polyether chain that is in Adiprene L-100, but it is terminated with an aliphatic diisocyanate, hydrogenated MDI. As this isocyanate is aliphatic, it can be cured at a reasonable rate with MDA; properties of the cured material are very similar to cured Adiprene L-100/MOCA, and it is claimed to have better hydrolytic stability than L-100/MOCA. Manufacturer's data are listed in Tables 4 and 5. It must be recognized that MDA is a liver toxin and possibly carcinogenic, although it is presently approved for use in dry bulk-food containers by the FDA.
2. Conathane EN-5, EN-7 (Conap Inc.). The prepolymer is a polybutadiene diol reacted with TDI, and it is cured with catalyzed polyol. The EN-7 system is said to be catalyzed with ferric acetylacetonate. The EN 4-7 series is said to have excellent adhesive properties, better than Adiprene L-100/MOCA. However, the cured polymer has somewhat lower hardness and modulus.

Table 3. Properties of some adhesives considered for use in weapons.

Name and manufacturer	Chemical type	Compat- ibility with HE and salt	Viscosity (cP)	Pot life (min)	Specific gravity	Shrink	Tensile strength (psi)	Shear strength (psi)	Brittle- ness temper- ature (°C)	Elon- gation at break (%)	Shore hardness
Adiprene LW-520 du Pont	Amine-cured polyether urethane	HE yes Salt yes	45,000	15-30	1.06	<1.3	4,700		<-94	350	90A
Conap EN-5,-7, Conap	Polyol-catalyst polybutadiene urethane		12,000	15-20	0.98	0.55	1,950			520	87A
Adiprene L-167 (polyol), du Pont	Polyol-cured poly- ether urethane		5,000		~1		3,000		<-95	470	62A
Adiprene L-315 (polyol), du Pont	Polyol-cured poly- ether urethane		15,000		~1		4,000+			350	90A
Castethane 2124, CPR-Upjohn	Polyol-cured polycaprolactone urethane	HE yes	880 at 100°C	15			5,000			320	80A
M-302 frothed adhesive, AEC	Epoxy-polyamide			30	0.3		~800				
Transfer adhesive 467(465,466), 3M		HE yes		Indefinite							
Aerobond 2017, Adhesive Engi- neering Co.	Modified epoxy (non-amine)			23	~1		~1,500	1,900 (lap shear)			
Neat 302, AEC	Epoxy-polyamide	PBX-9404		40	~1						25(Barcol)
Epoxy 828+13002	Epoxy-cyclic	PBX-9404		48	~1		10,000	2,800			12(Barcol)

Table 4. Properties of Adiprene LW-520 liquid-casting urethane elastomer.^a

Physical form	Viscous liquid
Color	Honey
Specific gravity at 25°C/4°C	1.03
Flash point (°F)	>550
Storage stability	Excellent in absence of moisture
Viscosity, Brookfield (cP)	
at 86°F	~45,000
at 212°F	~900
Available isocyanate content (%)	4.75 ± 0.15
Solubility	Soluble in aromatic hydrocarbons, ketones, esters, and chlorinated hydrocarbons

^aLW-520, a polyether-based liquid polymer, yields high-quality elastomers in the 90A Durometer hardness range when cured with LD-2729. LW-520 produces tough elastomers having excellent abrasion resistance and outstanding hydrolytic stability.

3. Castethane 2118 and 2124 (CPR Div., Upjohn). 2118 is an adipate polyester terminated with MDI and requires a catalyzed polyol curing agent. 2124 is a caprolactone polyester; it has better resistance to reversion in humid atmosphere. Both are compatible with PETN (Mound). CPR also has 1009-78, used in bonding HE at LASL, and an experimental compound, X-142-24-1, similar in hardness to Adiprene L-100/MOCA and said to have good resistance to reversion.
4. Adiprene L-167 or L-315 with polyol cure. Some work has been done with these systems. Catalysts such as triethylene diamine or ferric acetyl acetate are usually needed for adequate curing rates. L-315 will give hardness similar to L-100/MOCA but has lower modulus, elongation, and breaking strength.
5. Other proprietary urethane systems: Solithanes (Thiokol), Uralanes (Furane Plastics—some curing agents contain MOCA).
6. Epoxy/polyamide. Merginamide appears to be compatible with 9404. Some Versamides and others may also be compatible.
7. Silicone adhesives. Some of the addition systems have been used in solid-pack weapons. Modulus and strength are on the low side.

Table 5. Vulcanizate physical properties of Adiprene LW-520 cured with LD-2729.

	Typical value ^a
Compound	
LW-520 (4.75% NCO) (parts)	100
LD-2729 (95% theory) (parts)	10.6
Mixing and curing	
Mix temperature (°F)	212
Curing (hr/°F)	8-10/212
Conditioning in air at 75°F, 50% RH, before testing (days)	7
Working life (min)	4-6
Physical properties	
Hardness (Durometer A)	90
100% modulus (psi)	1,125
300% modulus (psi)	3,275
Tensile strength (psi)	4,700
Elongation at break (%)	350
Tear strength, ASTM D-470 (pli)	55
Abrasion resistance (NBS index)	1,275
Compression set (Method B, 22 hr at 158°F) (%)	65-70
Resilience, rebound (%)	40
Brittleness temperature (solenoid)(°F)	<-94
Torsional stiffness, Clash-Berg method (psi)	
75°F (24°C)	1,500
0°F (-18°C)	3,500
-40°F (-40°C)	8,500
-70°F (-57°C)	16,000
Specific gravity at 75°F	1.056
Linear shrinkage (%)	1.3

^aThe data shown are average values. A range of values can be expected because of normal deviations experienced in the routine testing of rubbers as well as the standard differences in the available NCO content of the polymer.

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