2cys

UCID - 16463

This is an informal report intended primarily for internal or limited external distribution. The opinions and conclusions stated are those of the author and may or may not be those of the laboratory.

LAWRENCE LIVERMORE LABORATORY

University of California/Livermore, California

PROPERTIES OF POSSIBLE ADIPRENE/MOCA REPLACEMENT MATERIALS

L. E. Peck
L. P. Althouse

March 28, 1974

NOTICE

This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Atomic Energy Commission, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights.

MASTER

Prepared for U. S. Atomic Energy Commission under contract no. W-7405-Eng-48

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

GG

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

PROPERTIES OF POSSIBLE ADIPRENE/MOCA REPLACEMENT MATERIALS

ABSTRACT

Seven adhesive formulations were evaluated as possible replacements for Adiprene L-100/MOCA formulation. Physical and chemical properties of the formulations are tabulated.

INTRODUCTION

As a result of Occupational Safety and Health Act (OSHA) restrictions¹ on the use of MOCA, * an adhesive based on an Adiprene L-100/MOCA formulation is no longer used. This adhesive was used widely within the AEC complex because of its chemical compatibility² with high explosives and its elastomeric properties. Seven substitute adhesive formulations³ are being evaluated as possible replacement adhesives. Properties being investigated include elemental analysis including halogen and spectrochemical ash, thermal coefficient of linear expansion (TCLE), gel time, maximum exotherm, time to exotherm, HE compatibility, T_g (glass point), ultimate rupture load in a butt-tensile geometry, and a 10 year adhesive aging study.

DISCUSSION

For adhesives used in nuclear weapons, properties such as elemental composition and high-explosive compatibility must be known in addition to the usual adhesive properties. Also, adhesive performance and aging properties must be reproducible within narrow limits.

Compositions of the seven substitute adhesives are given in Table 1. Formulations LPA 15 -35 through -37 are commercial resin systems purchased directly from the manufacturers.

Chemical elemental analysis as determined by both wet chemistry and spectrochemical analysis are listed in Table 2. Only elements present in quantities greater than 1 ppm are included in the tabulation. The halogen analysis refers to all the halogen elements but is reported as a chlorine analysis. Chlorine is usually the major halogen present in these polymeric materials.

MASTER

* 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. Identification and composition of seven resin systems.

Identification, LLL	LPA 15-32	LPA 15-33	LPA 15-34	LPA 15-35	LPA 15-36	LPA 15-37	LPA 15-38
Identification, Commercial				Canap EN-5	Canap EN-7	CPR 2124-80	
Composition (pbw)							
Adiprene L-315	100	100					100
Adiprene L-213			100				
1,4-butanediol	7	7	7				7
TMP	2	2	2				2
FeAcAc	0.03	0.02	0.03				
Part A				100	100	57.3	
Part B				17.5	17.5	42.6	
Dabco							0.02

Table 2. Properties of replacement adhesives.

Identification	LPA 15-32	LPA 15-33	LPA 15-34	LPA 15-35	LPA 15-36	LPA 15-37	LPA 15-38
Chemical analysis ^a (wt%)							
Carbon	5.72	5.74	5.66	3.87	3.83	3.78	5.79
Hydrogen	62.25	62.43	61.88	78.82	78.93	64.96	63.57
Nitrogen	8.45	8.46	8.43	9.45	9.54	7.50	8.61
Halogen ^b	0.03	0.03	0.04	<0.01	0.1	0.02	0.03
Ash ^b	0.03	0.02	0.009	0.019	0.009	0.002	0.032
Spectrochemical analysis ^c (ppm)							
Silicon	40	8	8	10	15	7	10
Fe	20	10	15	3	9	—	10
Tin	1	2	—	15	5	—	10
Aluminum	7	—	—	—	—	—	—
Calcium	5	—	—	1	1	—	1
Boron	—	—	—	1	1	—	—
Lead	1	1	—	1	—	—	—
Magnesium	1	—	—	—	—	—	—
Gel time (min)	92	128	80	24	67	10	61
Peak exotherm (°C)	39	35	39	55	47	120	43
Time to peak exotherm (min)	35	35	23	15	20	6	25

^aFrom Ref. 4.^bFrom Ref. 5.^cFrom Ref. 6.

Gel time refers to a gelation stage during the adhesive cure cycle. Gel time was measured in minutes using an adhesive mass of 50 g. The exothermic nature of room temperature cure adhesives is illustrated by formulation LPA 15-37 with a peak exotherm of 120°C within 6 min and a gel time of 10 min. All gel-time measurements were made on a Gardner Company MOL-REZ gel timer. Peak exotherm temperature and time are both tabulated in Table 2 and plotted as Fig. 1. The useful time in minutes of these adhesives in a 50-g mass correlates better with peak exotherm times than with gel times.

Doctorability of the various adhesive formulations was judged by extruding an 0.0254-cm (0.010-in.) film with a Gardner knife Model 3-31 doctor blade. All formulations except LPA 15-37 were considered acceptable for doctor blade application.

Density and TCLE properties were determined. The TCLE measurements were made by a volume displacement technique.⁷ Thermal coefficient measurements were determined over the range of -35 to +75°C.

Adhesive properties were determined in a butt-tensile geometry. A bond gap of 0.0254 cm (0.010 in.) and a tensile testing rate of 0.10 cm/min (0.04 in./min) were held constant. A summary of ultimate rupture butt-tensile load is given in Table 3. Rupture loads plotted against time are provided (Figs. 2-13).

The validity of adhesive aging data depends on the ability of the investigator to discriminate between the usual aging variation and other time-induced variations. The reproducibility of the adhesive system is first determined by bonding 50 adhesive coupons. The coupons are divided into 10 groups of five coupons. Statistical quality control limits are calculated for both the mean and the range of ultimate rupture load values. These confidence limits are then used to judge aging data. All the control group coupons were cured for 6 hr at 100°C (212°F). Aging adhesive coupons are cured and tested at 22°C (72°F) and stored in a 10% relative humidity atmosphere during aging.

Fig. 1. Peak exotherm versus time for various urethane systems.

Table 3. Butt-tensile ultimate rupture stress of replacement adhesives.

Identification	LPA 15-32	LPA 15-33	LPA 15-34	LPA 15-35	LPA 15-35	LPA 15-37	LPA 15-38
Confidence limits							
Stuck bond No.	437(1-50)	440(1-50)	439(1-50)	446(51-99)	446(1-50)	449(1-50) ^b	444(46-76)
Mean (MPa)	23.26-21.31	21.63-17.41	20.33-19.26	16.94-15.93	17.74-16.96	1.75-1.36	NA ^a
Range (MPa)	4.25-0.955	10.11- 2.06	2.67-0.544	2.42-0.499	1.86-0.388	0.93-0.19	NA
Aging data							
Stuck bond No.	442(1-60)	432(1-60)	443(1-60)	448(1-60)	447(1-60)	450(1-60)	NA
Bond age, days	89	120	88	41	41	41	NA
Mean (MPa)	20.27	10.87	16.92	16.68	16.75	6.50	NA
Range (MPa)	2.44	7.74	3.04	1.21	1.21	1.37	NA
Coeff. var. (%)	5	33	7	5	8	9	NA
TCLE (10 ³)	1.10	1.109	1.116	1.122	1.133	1.084	1.101
Density (g/cm ³)	1.47	1.145	1.148	1.004	1.008	1.108	1.144

^aNA indicates confidence limits unacceptable for aging study.^bMaterial degradation during elevated temperature cure.

Fig. 2. Adhesive aging study for bond number 442; (a) range control chart, (b) mean control chart.

Test program												
Test increment No.	1	2	3	4	5	6	7	8	9	10	11	12
Bond sub-numbers	1-5	6-10	11-15	16-20	21-25	26-30	31-35	36-40	41-45	46-50	51-55	56-60
Test date	10-25-73	10-27-73	10-29-73	11- 5-73	11-13-73	12- 5-73	1-22-74					
Bond age (days)	0	2	4	11	19	41	89					
Bond age (years)	0	0.01	0.01	0.03	0.05	0.11	0.24					
Test results												
Mean rupture load (MPa)	2.17	10.36	13.38	17.31	18.71	20.36	20.27					
Range (MPa)	0.36	2.90	1.06	1.83	0.91	1.22	2.44					
Coeff. of variation	6	11	3	4	2	3	5					

Fig. 3. Adhesive aging study for bond number 442; aging data and projection.

Fig. 4. Adhesive aging study for bond number 432; (a) range control chart, (b) mean control chart.

Test program												
Test increment No.	1	2	3	4	5	6	7	8	9	10	11	12
Bond sub-numbers	1-5	6-10	11-15	16-20	21-25	26-30	31-35	36-40	41-45	46-50	51-55	56-60
Test date	8-30-73	9- 1-73	9- 3-73	9- 7-73	9-18-73	10- 1-73	10-30-73	12-28-73				
Bond age (days)	0	2	4	8	19	32	61	120				
Bond age (years)	0	0.01	0.01	0.02	0.05	0.09	0.17	0.33				
Test results												
Mean rupture load (MPa)	0.17	8.80	7.18	6.89	6.07	8.42	5.64	10.87				
Range (MPa)	0.17	10.78	5.01	7.13	7.89	7.43	5.01	7.74				
Coeff. of variation	42	46	28	48	59	36	33	33				

Fig. 5. Adhesive aging study for bond number 432; aging data and projection.

Fig. 6. Adhesive aging study for bond number 443; (a) range control chart, (b) mean control chart.

Test program

Test increment No.	1	2	3	4	5	6	7	8	9	10	11	12
Bond sub-numbers	1-5	6-10	11-15	16-20	21-25	26-30	31-35	36-40	41-45	46-50	51-55	56-60
Test date	10-26-73	10-28-73	10-30-73	11- 5-73	11-14-73	12- 6-73	1-23-74					
Bond age (days)	0	?	4	10	10	11	00					
Bond age (years)	0	0.01	0.01	0.03	0.05	0.11	0.24					

Test results

Mean rupture load (MPa)	1.52	6.97	11.41	13.55	15.16	16.62	16.92
Range (MPa)	0.21	1.59	3.04	1.21	0.91	0.30	3.04
Coeff. of variation	5	9	12	4	3	1	7

Fig. 7. Adhesive aging study for bond number 443; aging data and projection.

Fig. 8. Adhesive aging study for bond number 448; (a) range control chart, (b) mean control chart.

Test program												
Test increment No.	1	2	3	4	5	6	7	8	9	10	11	12
Bond sub-numbers	1-5	6-10	11-15	16-20	21-25	26-30	31-35	36-40	41-45	46-50	51-55	56-60
Test date	1-16-74	1-18-74	1-20-74	1-25-74	2- 4-74	2-26-74						
Bond age (days)	.0	2	4	9	19	41						
Bond age (years)	0	0.01	0.01	0.02	0.05	0.11						
Test results												
Mean rupture load (MPa)	4.50	10.56	12.63	14.34	15.04	16.68						
Range (MPa)	0.76	0.91	0.91	1.52	0.91	1.21						
Coeff. of variation	7	3	3	5	2	3						

Fig. 9. Adhesive aging study for bond number 448; aging data and projection.

Fig. 10. Adhesive aging study for bond number 447; (a) range control chart, (b) mean control chart.

Test program

Test increment No.	1	2	3	4	5	6	7	8	9	10	11	12
Bond sub-numbers	1-5	6-10	11-15	16-20	21-25	26-30	31-35	36-40	41-45	46-50	51-55	56-60
Test date	1-15-74	1-18-74	1-20-74	1-24-74	2- 4-74	2-25-74						
Bond age (days)	0	3	5	9	20	41						
Bond age (years)	0	0.01	0.01	0.02	0.05	0.11						

Test results

Mean rupture load (MPa)	0.76	3.56	7.05	10.56	14.46	16.75						
Range (MPa)	0.08	0.68	1.21	1.52	1.37	1.21						
Coeff. of variation	5	8	7	6	4	3						

Fig. 11. Adhesive aging study for bond number 447; aging data and projection.

Fig. 12. Adhesive aging study for bond number 450; (a) range control chart, (b) mean control chart (material degradation during elevated temperature cure).

Test program											
Test increment No.	1	2	3	4	5	6	7	8	9	10	11 12
Bond sub-numbers	1-5	6-10	11-15	16-20	21-25	26-30	31-35	36-40	41-45	46-50	51-55 56-60
Test date	1-15-74	1-17-74	1-20-74	1-24-74	2- 4-74	2-25-74					
Bond age (days)	0	2	5	9	20	41					
Bond age (years)	0	0.01	0.01	0.02	0.05	0.11					
Test results											
Mean rupture load (MPa)	2.67	4.81	5.29	6.12	6.50	6.50					
Range (MPa)	0.45	0.45	1.59	1.13	0.91	1.37					
Coeff. of variation	7	4	13	9	6	9					

Fig. 13. Adhesive aging study for bond number 450; aging data and projection.

REFERENCES

1. Environmental Impact Statement Issued by OSHA on May 3, 1973, Dept. of Labor, Washington, D.C.
2. LLL High Explosive Handbook, Lawrence Livermore Laboratory, Rept. UCRL-6759 (1967), pp. 1-3.
3. H. G. Hammon, Properties of Adiprene L-100/MOCA as a Room Temperature Cure Adhesive and Possible Substitutes for It, Lawrence Livermore Laboratory, Rept. UCID-16329 (1973).
4. Lawrence Livermore Laboratory, Internal Document (Analytical Chemistry Rept.) V3126 (1974). Readers outside the Laboratory who desire further information on LLL internal documents should address their inquiries to the Technical Information Department, Lawrence Livermore Laboratory, Livermore, California 94550.
5. Lawrence Livermore Laboratory, Internal Document (Analytical Chemistry Rept.) CSN-10442 (1974).
6. Lawrence Livermore Laboratory, Internal Document (Analytical Chemistry Rept.) Plate 3150 (1974).
7. Lawrence Livermore Laboratory, Internal Document Lab. Ref. 7-21, Job No. 240273 (1974).

DISTRIBUTION

LLL Internal Distribution

G. D. Dorough/H. Rizzo
 J. W. Frazer/L. W. Roberts
 E. R. Bissell/F. Walker
 H. G. Hammon
 P. G. Fleming
 B. Garner
 W. E. Nelson
 D. F. Cruff
 L. E. Peck
 W. E. Cady
 E. S. Jessop
 A. T. Buckner
 J. K. Lepper
 H. Wilson
 R. Wasley
 R. Brady
 D. Seaton
 C. Bender
 TID File

10

30

F. Childress
 H. Kite
 Union Carbide Corporation
 Oak Ridge, TN

F. Jackson
 R. Frohmberg
 C. Smith, Jr.
 The Bendix Corporation
 Kansas City, MO

P. Rand
 J. McDonald
 Sandia Laboratories
 Albuquerque, NM

D. Adolphson
 Sandia Laboratories
 Livermore, CA

L. Hartzel
 Monsanto Research Corporation
 Miamisburg, Ohio

R. Spray
 Mason and Hanger-Silas
 Mason Co., Inc.
 Amarillo, TX

Technical Information Center
 Oak Ridge, TN

2

External Distribution

W. May
 F. Dubois
 Los Alamos Scientific Laboratory
 Los Alamos, NM

NOTICE:

"This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Atomic Energy Commission, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately-owned rights."