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EVALUATION OF ADHESIVES FOR USE IN THE
HI FRAG 5 INCH/54 PROJECTILE

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22 January 1975

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systems and the effect of thermal aging on the fabricated adhesive joints are discussed. Recommendations are made concerning the choice of optimal beaker and adhesive materials for use in the Hi-Frag projectile.

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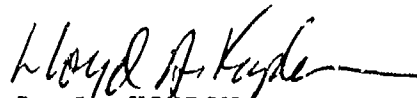
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EVALUATION OF ADHESIVES FOR USE IN THE HI FRAG
5"/54 PROJECTILE

This report describes the adhesive bonding characteristics of an epoxy adhesive, a urethane adhesive and an explosive, PBXN-106, with three polymers, polyethylene, nylon, and ethyl cellulose. These materials are being evaluated for possible use in the HI-FRAG two piece projectile program. This work was supported under Task 897-NWL with funds from NAVSURFWPCEN/Dahlgren Work Order Number PO 4-0026.

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INTRODUCTION

Problem Description and Study Objectives

The Naval Surface Weapons Center, Dahlgren (NAVSURFWPNCEN) is developing a family of new improved 5" High Fragmentation (Hi-Frag) Projectiles. The new projectile features a two piece body design with a pressed fit joint and an explosive encapsulating polymeric beaker [1] as shown in Figure 1. The explosive currently used in these projectiles is PBXN-106, a castable RDX/polyurethane high explosive [2]. The main explosive charge, rather than being cast directly into the projectile cavity as in conventional projectile production, is first cast into the polymeric beaker which is then inserted into the projectile cavity during the projectile assembly process.

Use of this explosive-beaker combination offers a number of advantages over the conventional loading technique. Besides improving explosive inspection, disassembly and disposal operations, the beaker also prevents any contact between the projectile wall and the explosive, and if necessary, may be readily adapted so as to hermetically seal the explosive charge. When employing the explosive-beaker combination, however, care must be exercised to prevent the formation of air gaps at the explosive/beaker and beaker/projectile interfaces, since adiabatic compression of these gaps during gun firing may result in premature initiation of the explosive. These air gaps may be present for a number of reasons, namely ullage due to dimensional tolerances between the fabricated beaker and the projectile, differences in thermal expansion between the explosive and beaker and beaker and steel, and via handling and transportation of the as assembled projectile.

The four polymeric beaker materials listed in Table 1 have been proposed as candidate beaker materials. The proposed application requires certain qualities of a beaker material. First and

¹Grittner, Gary J., "5"/54 Caliber High Fragmentation Projectile Explosive Encapsulant Beaker - Material Selection for Engineering Gunfire Tests", Naval Weapons Laboratory Technical Report 3032, November 1973

²Heller, H., Bertram, A., Elban, W., Ringbloom, V., "PBXW-106, A New Impact Insensitive, Heat Resistant Castable Explosive", Naval Ordnance Laboratory Technical Report No. 72-86 (July 1972)

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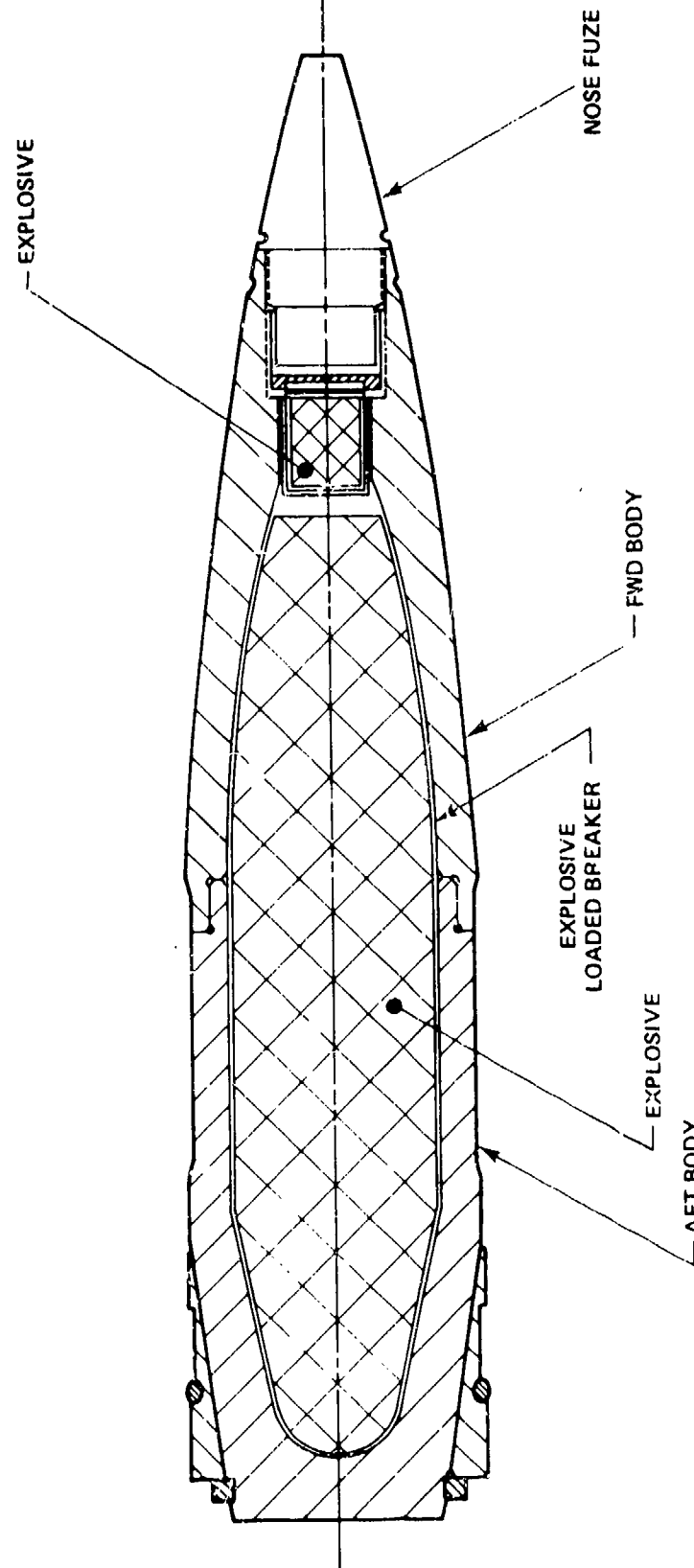


FIG. 1 NEW 5"/54 PROJECTILE DESIGN

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Table 1

CANDIDATE BEAKER MATERIALS

Polyethylene

CL-50* Cross-linked, untreated and surface flame treated

CL-100* Cross-linked, untreated and surface flame treated

Nylon 12

Ethyl Cellulose

*Registered Trademark of Phillips Petroleum Company

foremost, the polymeric material of the beaker must be chemically compatible with the explosive charge, since the beaker will be in intimate contact with the explosive. Second, to prevent gaps at the explosive/beaker interface, the explosive, PBXN-106, must adhere to the walls of the beaker. Any bond present at this interface should be sufficient to overcome the effect of the minor differences in thermal expansion coefficient between the various candidate beaker materials and PBXN-106, Table 2. Third, to prevent gap formation at the beaker-steel interface, it must be possible to adhesively bond the beaker to the projectile, thereby, effectively eliminating the source of gaps, i.e., separation of the beaker from the projectile wall. Fourth, the beaker material must retain these qualities over the life span of the projectile, which may approach 10 to 20 years.

In light of the above requirements, the Naval Surface Weapons Center, White Oak (NAVSURFWPNCEN), was tasked by NAVSURFWPNCEN/Dahlgren to evaluate the adhesive bonding characteristics of the candidate beaker materials of Table 1 with PBXN-106 and various adhesives.

Mechanism of Adhesion

In general, the formation of an adhesive joint may be thought to have the following characteristics: (1) a liquid adhesive, (2) intimately contacts surfaces to be bonded, (3) forms a strong solid which, (4) attracts and holds the surfaces effectively. Characteristics (1) and (3) will depend only on the inherent properties of the specific adhesive material. Characteristics (2) and (4), however, are inherent in all adhesive joints and hence require further investigation. These two characteristics are discussed in reverse order below.

The two mechanisms by which adhesives attract components (adherends) are mechanical and chemical adhesion. Mechanical adhesion is that portion of the adhesive strength which results from

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Table 2

THERMAL EXPANSION COEFFICIENTS

Material	Thermal Expansion Coefficient cm/cm/°C x 10 ⁴
PBXN-106	1.2
Polyethylene	1-2
Nylon	1
Ethyl Cellulose	1-2
Steel	0.11-0.16

the mechanical interlocking of the adhesive in the pores of the adherends. The walls of these pores are usually thin, hence, the adhesive must be rigid and strong if additional strength is to be achieved. Polymers usually have smooth, non-porous surfaces and the pore walls are somewhat flexible when thin. For these reasons, polymers typically do not gain much adhesive strength via this mechanism.

Chemical adhesion arises from the formation of an intimate bond between the chemical species of the adhesive and adherend. The mechanisms primarily responsible are: 1) primary bonding resulting from the chemical reaction between adhesive and adherend with the resultant formation of an ionic or covalent bond, and 2) secondary or Van der Waals bonding due to the attraction of electrically positive and negative sites (polar sites) on the surface of the adhesive and adherends. These polar sites result from the separation of the centers of positive and negative charges in an electrically neutral molecule. For polymeric materials, when carbon or hydrogen sites are occupied by oxygen, nitrogen, hydroxyl groups etc., such sites will appear more polar due to the higher electron attracting affinity of these atoms. These polar areas in the adhesive and adherend when properly aligned exert an unlike charge attraction for each other and hence adhere. When the molecules are small, these forces are usually insufficient to produce appreciable bonding. However, the effects of these attractive forces becomes quite large when the molecules are large, as for polymers, and may approach the strength achieved through formation of a primary bond. The relative polarities of several typical materials are listed in Table 3.

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Table 3

RELATIVE POLARITY OF VARIOUS MATERIALS [5]

Low	Medium	High
Metals	Metal oxides	Paper
Plastics	Plastics	Fabric
Polyethylene	Acrylics	Wood
Polypropylene	Epoxy	Plastic
Polyvinyl chloride	Polyvinyl butyral	Polyvinyl alcohol
Teflon	Polyvinyl acetate	Polyesters
Rubber	Rubbers	Cellulose esters
Natural	Nitriles	Urea
SBR	Polysulfides	Melamine
	Silicones	Nylon
		Sodium Silicate

Polyethylene and Teflon are seen to be of very low relative surface polarity. In order to bond these materials effectively the chemical reactivity of the polymer chains at the surface must be modified. This can be done by techniques like flame treating[3], acid etching[4], or by irradiation[4]. These techniques bring about a reaction between the polymeric surface molecules and oxygen in the air, which results in the incorporation of the oxygen atoms into the chemical structure of the surface molecules, thereby, increasing the polarity and adhesibility.

The second characteristic to be considered in the formation of an adhesive joint is the intimate contact required between adhesive and adherend. Three factors are of particular importance in achieving this intimate contact: 1) the liquid adhesive must wet the surface of the substrate, 2) the surface of the substrate must be free of contamination, and 3) the adhesive must be fluid enough to flow out and conform to the shape of the substrate surface. The effects of the latter two factors are self-evident. Good wetting results when there are strong attractions between the molecules of the adhesive and substrate. Polarity plays an important role in the wetting ability of most liquid adhesives, since in general if the surface is very polar it will attract the molecules of the adhesive and hence cause the liquid adhesive to wet the surface.

³ Dixon, A. T., Bodnar, M. J., "Effects of Various Surface Treatments on Adhesive Bonding of Polyethylene", Adhesives Age, p. 35 (May 1969)

⁴ Schonhorn, H., Ryan F. W., "Surface Crosslinking of Polyethylene and Adhesive Joint Strength", J. App. Polymer Science, 18, p. 235 (1974)

⁵ Katz, I., "Adhesive Materials, Their Properties and Usage", Foster Publishing Co. Calif., 1964, p. 2

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COMPATIBILITY OF CANDIDATE BEAKER MATERIALS AND PBXN-106

The chemical compatibility of the candidate beaker materials and PBXN-106 was examined using two accelerated tests, vacuum gas evolution and nitroplasticizer absorption. These accelerated tests act as analogs to actual long term storage of an explosive in contact with a particular material, and allow prediction of possible long term incompatibility after a relatively short testing period.

The vacuum thermal stability test procedure as specified by Simmons[6] was used to determine any significant gas evolution in the tested systems. The test results obtained permit evaluation of each system on a pass-fail basis with gas evolution of greater than 2 ml/g/48 hours at 100°C indicating incompatibility.

The experimental arrangement used to determine the degree of nitroplasticizer absorption by the candidate beaker materials is shown in Figure 2. The procedure used in the determination was as follows: a 100 mm by 25 mm polymer sample of known weight was immersed in nitroplasticizer for a period of 300 hours or more at 71°C, wiped dry, rinsed with acetone (to remove any residual nitroplasticizer) and reweighed. Absorption of nitroplasticizer causes a weight increase of the specimen. Generally, greater than a 5% weight increase is considered a failure.

The result obtained for the above compatibility determinations are presented in Table 4. The results indicate that all candidate beaker materials are compatible with PBXN-106. The negative values obtained for the nitroplasticizer absorption test are indicative of a net weight loss. Since there is no definitive technique to establish the absolute cause of this weight change, it is felt that these numbers imply either a slight solubility of the polymers in the nitroplasticizer, or experimental error. This solubility is small (since a value as low as 0.5% would appear as a distortion of the sample surface and no distortion was evident) and is not believed to be significant.

⁶Simmons, H. T., "The Vacuum Thermal Stability Test for Explosives", Naval Ordnance Laboratory Technical Report No. 70-142, 28 October 1970

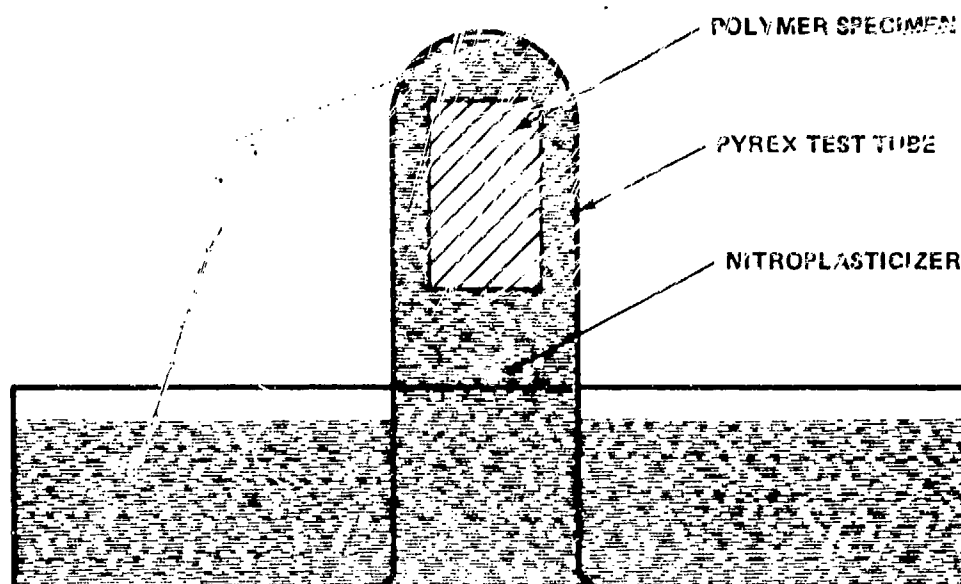


FIG. 2 NITROPLASTICIZER ABSORPTION TEST CONFIGURATION

Table 4
CHEMICAL COMPATIBILITY OF THE
CANDIDATE BEAKER MATERIALS WITH PBXN-106

Material	Vacuum Gas Evolution ml/g-sample/48 hours at 100°C	Nitroplasticizer Absorption & weight change	Chemical Compatibility Criterion
CL-50 Untreated	0.33	-0.04	Pass
CL-50 Surface Flame Treated	0.59	-0.05	Pass
CL-100 Untreated	0.18	-0.11	Pass
CL-100 Surface Flame Treated	0.51	-0.10	Pass
Ethyl Cellulose	0.09	-0.07	Pass
Nylon 12	0.28	-0.01	Pass

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BOND STRENGTH MEASUREMENTS

Sample Preparation and Testing Procedure

The single joint overlap test configuration, as shown in Figure 3, was chosen for the bond strength measurement since it best simulates the in service configuration of the projectile, beaker, adhesive, and explosive materials.

The test specimens were prepared as follows: 25 mm by 103 mm polymer test strips were cut from polyethylene plates (Phillips) and from Nylon-12 and ethyl cellulose beakers using a guillotine. The nylon and polyethylene strips were then degreased using 1,1,1-trichloroethylene (trichlor). Warm soapy water in an ultrasonic cleaner was used to clean the ethyl cellulose test strips.

Due to the non-uniform thickness of the as received ethyl cellulose, some additional preparation was required before adhesive joint formation. Preliminary tests showed that the thin areas of the test strips failed before adhesive joint failure occurred. In order to increase the strength of these thin areas, and shift the failure point to the adhesive joint, the ethyl cellulose strips were laminated to 1/32-inch cold rolled steel strips using Armstrong A-271 epoxy adhesive prior to adhesive joint formation.

The steel strips used to simulate the wall of the projectile in the adhesive joint were cut from 1/32-inch cold rolled steel, degreased using trichlor, dried and rinsed with clean trichlor. In the actual projectile, the inside wall is coated with a primer material to protect the metal from oxidation. The beaker therefore is adhesively bonded not to steel but rather to this primer material. To insure an adequate representation of the "in service" configuration, the steel strips were coated with the recommended primer material, FM-47 (a vinyl phenolic primer), before adhesive joint formation. Three primer coatings were applied by dipping the steel strips into the primer, with a 24-hour drying period between each application.

Formation of the adhesive joints was then accomplished as follows. A thin layer of the adhesive was applied to the coated steel strip. The polymer strip was then clamped to the steel strip to insure a 13 mm joint overlap and a continuous, uniform adhesive layer between test strips. Excess adhesive was removed before cure.

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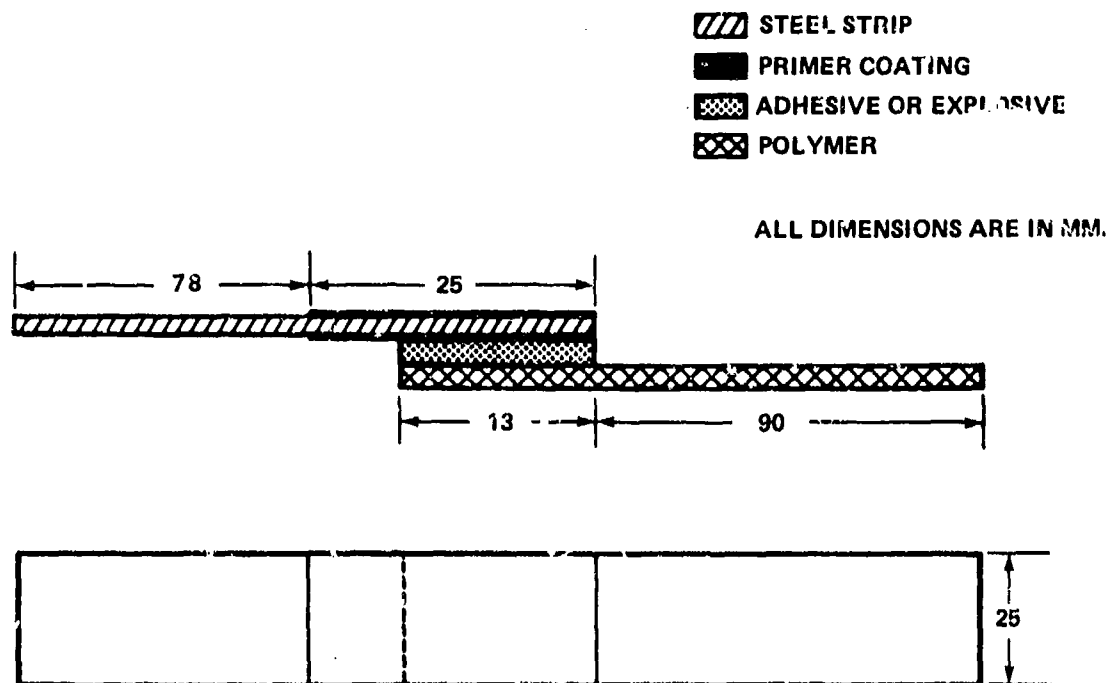


FIG. 3 SINGLE JOINT OVERLAP TEST CONFIGURATION

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The clamped adhesive samples were then allowed to cure at $23 \pm 2^{\circ}\text{C}$ for 48 hours before any subsequent aging or testing. The thickness of the adhesive layer was typically 0.01 mm.

The explosive joints were cast in such a way so as to insure a 3 mm layer of explosive between the polymer and steel test strips. Two batches of explosive were used, mix numbers 71-S and 74-E, to cast all test samples. After allowing the explosive to cure at $23 \pm 2^{\circ}\text{C}$ for 48 hours the excess explosive was removed to produce an explosive joint of dimensions 25 mm x 13 mm x 3 mm.

Two sets of explosive joints and adhesive joints were fabricated for each candidate beaker material to be tested. One set of fabricated joints was thermally cycled before the bond strength measurements were performed, while the other set was tested immediately after curing. This was done so that the effect of thermal aging on the adhesive or explosive bond strength could be determined. The thermal aging cycle which was used consisted of twenty-eight (28) - four (4) hour cycles from 71°C to -54°C followed by a prolonged thermal age, thirty-two (32) hours, at 71°C and -54°C . Metal desiccators were used to control the environment during thermal aging.

Bond strength measurements using an Instron Universal Tester in accordance with the testing method specified in ASTM D-1002 were made with the following modifications:

- 1) Each test joint was constructed individually rather than in units of five.
- 2) One test strip of the fabricated joint was the particular polymer material under consideration and the other test strip was 1/32 inch cold rolled steel.
- 3) Only five samples of each configuration were tested due to material limitations.
- 4) The free cross-head testing speed was 0.2 cm/min rather than the recommended 0.13 cm/min due to equipment limitations.

Preliminary Materials Evaluation

Before the bond strength measurements were performed the candidate beaker materials (Table 1) and a number of adhesives were qualitatively evaluated as to their possible value in the program.

Adhesive Selection

The adhesives which underwent this preliminary evaluation are listed in Table 5. These materials represent two general classes of adhesives, epoxy type and urethane type. Other classes, i.e.

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Table 5

PRELIMINARY ADHESIVES EVALUATED

Epoxy

Epoxy Patch Kit 1C White (Hysol Division of Dexter Corporation)
Armstrong A-271 (Armstrong Products Co., Inc.)
Chemlok 304 (Hughson Chemicals)
Chemlok 305 (Standard mix ratio) (Hughson Chemicals)
Chemlok 305 (Alternate mix ratio) (Hughson Chemicals)

Urethane

Adiprene L-100 (DuPont), Butanediol-Trimethylolpropane Cure
Adiprene L-100 (DuPont), Butanediol-Hexanetriol Cure
Poly bd R-45M* (ARCO), Toluenediisocyanate (TDI) Cure
Poly bd R-45M (ARCO), Hexatriacontanediisocyanate (DDI) Cure

*Registered Trademark of Atlantic Richfield Company Polybutadiene

anaerobic adhesives, hot melt adhesives etc., were not considered suitable for this application due to such factors as high material cost, high temperature requirements and unusual adherend preparation requirements.

It is believed that the chosen adhesives should possess certain qualities:

- 1) It must be somewhat fluid and allow easy processing and application.
- 2) It must form an adequate bond with only a room temperature cure.
- 3) The cured adhesive must be somewhat flexible, since it is felt that a flexible rather than a brittle material would better withstand the constant jolting and impacting inherent in the handling of a large mass, and accommodate the strains produced during thermal cycling. These strains result from the large difference in thermal expansion coefficient between steel and the beaker materials, table 2.
- 4) The uncured and cured adhesive must be non-toxic and require a minimum amount of precaution in its use.

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All of the adhesives of Table 5 were evaluated under these guidelines. With the exception of Hysol's Epoxy Patch kit all of the epoxies were easily processed and applied and produced essentially equivalent properties. Hysol's epoxy adhesive was extremely viscous and would not be easily processable in a large batch, hence it was eliminated from further investigation. Of the remaining epoxies, only Chemlok 305 (alternate mix ratio) produced a somewhat flexible material and retained the high bond strength typical of epoxies. Due to the added flexibility obtained this material was chosen for further study.

Of the four urethane type adhesives listed in Table 5, the DDI cure of ARCO's R-45M was chosen as another candidate adhesive. This system was chosen over the TDI cure of R-45M due to the known toxicity of TDI⁷ and the added moisture resistance obtained with a DDI cure. The two cures of Dupont's Adiprene L-100 were also eliminated from further consideration due to their high viscosity at room temperature which prevented adequate processing and degassing of entrapped air and gas. In summary, the two adhesives which were chosen for further study were Chemlok 305 (alternate mix ratio) and the DDI cure of ARCO's R-45M poly bd. The mixing ratios for the two adhesives are given in Table 6.

Polymer Selection

Two polyethylene materials have been proposed as candidate beaker materials, Phillips CL-50 and CL-100. Chemically these polymers differ only in the degree of cross-linking present across the polymer chains, with CL-100 being the more highly cross-linked material. This difference in cross-linking should have a marked effect upon the inherent mechanical properties and cohesive strength of the polymers, however, it is questionable if any significant difference in the adhesive bonding characteristics would also occur. A more significant increase in adhesive bonding should be obtained via a surface flame treatment of each of the polyethylene materials.

To determine the effect of cross-linking vs surface flame treatment of polyethylene, adhesive joints were prepared in the manner outlined above using Chemlok 305 (alternate mix ratio) and the adhesive bond strengths measured. The results of the measurements are presented in Table 7. Two conclusions are immediately obvious: 1) additional cross-linking has no significant effect on adhesion to polyethylene, and 2) surface flame treatment increases the adhesive strength of polyethylene joints by almost a factor of three. For this reason only one cross-linked polyethylene material will undergo further examination, Phillips CL-50. This material was selected because of lower cost and better thermal expansion coefficient match with PBXN-106 when compared to CL-100^[2].

⁷"Toluene Diisocyanate", Chemical Safety Data Sheet, SD-73, Manufacturing Chemistry Association, Washington, D.C.

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Table 6

MIXING RATIO FOR EPOXY AND URETHANE ADHESIVES

Chemlok 305[8]

1 part by weight part 1
2 parts by weight part 2
Pot life approximately 1½-2 hours at 23°C

DDI cured R-45M

100 parts by weight R-45M
33.3 parts by weight DDI
0.05 parts by weight dibutyltindilaurate per 100 parts R-45M
Pot life approximately 2 hours at 23°C

Table 7

PHILLIPS POLYETHYLENE
PRELIMINARY BOND STRENGTH MEASUREMENTS
WITH CHEMLOK 305 (ALTERNATE MIX RATIO) ADHESIVE

Polymer	Bond Strength	
	kg/cm ²	Psi
CL-50 untreated	9.35	133
CL-100 untreated	9.30	132
CL-50 Surface Flame Treated	26.3	373
CL-100 Surface Flame Treated	26.0	370

⁸ Hughson Chemicals, Product Information Technical Bulletin No. 3017A

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Explosive Bond Strength Measurements

Table 8 contains the results of the bond strength measurements on the cast explosive joints. The bond strengths are seen to vary between 1.08 Kg/cm² and 2.12 Kg/cm² indicating that PBXN-106 will adhere to a polymer beaker upon casting. The minor differences in bond strength in the table are probably not the result of increased or decreased adhesion but rather slight differences between the two batches of PBXN-106, Numbers 71S and 74E, used to cast the arrangement.

Failure of these explosive joints was always by a tear-type separation very near the PBXN-106 polymer interfaces. Further examination revealed that a thin film of explosive binder was retained on the polymer surface. The explanation for this is unclear but it is postulated that a very thin binder-rich layer is formed at the polymer surface upon casting the explosive. This low solids content layer is weaker than either the bond to the polymer surface or the surrounding material and hence was the first to fail. The assumption of a binder-rich layer is further supported by the fact that the measured bond strengths are slightly greater than the reported tensile strength of the binder, 1.48 Kg/cm² [9], but are significantly less than the tensile strength of PBXN-106, 3.24 Kg/cm² [2].

The data of Table 8 also indicate that the thermal aging cycle had essentially no effect on the bond strengths.

Adhesive Bond Strength Measurements

The results of the adhesive bond strength measurements using Chemlok 305 (alternate mix ratio) and the DDI cure of ARCO's R-45M are tabulated in Tables 9 and 10. Included in these tables are the failure modes and number of failures by each mode. No data was reported in table 9 for two arrangements,

CL-50 / Chemlok / FM-47 coated
untreated / 305 / steel

and

Nylon 12 / Chemlok / FM-47 coated
305 / steel

after thermal aging, because each of the test specimens failed before the bond strength measurements could be performed. The cause for this behavior is discussed later in this section when the effects of thermal aging are discussed.

⁹Goldhagen, S., Rothenstein, J., Melin, D. H., "Development of New High Energy Explosive Compositions", Aerojet General Corporation Report No. 1174-81-Q7, p. 25 (April 1969)

Table 8
EXPLOSIVE BOND STRENGTHS MEASUREMENTS

Polymeric Beaker Materials	Explosive Batch No. Unaged Aged	Bond Strength		Failure Mode
		Kg/cm ²	psi	
CL-50 Untreated	71-S 74-E	1.18	16.8	27.7
		$\sigma^*=0.1$	$\sigma=1.5$	$\sigma=0.06$ $\sigma=0.9$
CL-50 Surface Flame Treated	71-S 74-E	1.08	15.4	30.1
		$\sigma=0.1$	$\sigma=1.4$	$\sigma=0.06$ $\sigma=0.9$
Nylon 12	74-E 74-E	1.95	27.7	26.3
		$\sigma=0.08$	$\sigma=1.16$	$\sigma=0.13$ $\sigma=1.8$
Ethyl Cellulose	74-E 74-E	1.94	27.6	24.9
		$\sigma=0.11$	$\sigma=1.54$	$\sigma=0.15$ $\sigma=2.2$

σ^d = Standard
deviation

Table 9
ADHESIVE BOND STRENGTH MEASUREMENTS
USING CHEMLOK 305 EPOXY ADHESIVE

Polymeric Beaker Material	Prior Thermal Treatment	Bond Strength Kg/cm ²	Bond Strength (Psi)	Failure Mode
CL-50 untreated	None	9.0 $\sigma=2.1$	128 $\sigma=29$	5 Adhesive/Polyethylene Interface Failures
	Thermal Aging	-	-	All bonds broken before testing
CL-50 Surface Flame Treated	None	29.4 $\sigma=4.2$	417 $\sigma=59$	5 Adhesive/Polyethylene Interface Failures
	Thermal Aging	2.2 $\sigma=1/0$	31. 15.	5 Adhesive/Polyethylene Interface Failures
Nylon 12	None	30.4 $\sigma=6.8$	432 $\sigma=96$	4 Adhesive/Nylon Interface Failures 1 Nylon Failures
	Thermal Aging	-	-	All bonds broken before testing
Ethyl Cellulose	None	54.4 $\sigma=3.7$	773 $\sigma=53$	1 Ethyl Cellulose Failure 3 Adhesive Failures 1 Adhesive/Ethyl Cellulose Failure
	Thermal Aging	73.4 $\sigma=6.7$	1044 $\sigma=96$	2 Adhesive Failures 2 Ethyl Cellulose Failures

* σ $\pm$ standard deviation

Table 10
ADHESIVE BOND STRENGTH MEASUREMENTS USING A
DDI CURED R-45M ADHESIVE

Polymeric Beaker Materials	Prior Thermal Treatment	Bond ₂ Strength Kg/cm ²	Psi	Failure Mode
CL-50 untreated	None	2.3	32	5 Adhesive/Polyethylene Interface Failures
		$\sigma^*=0.27$	$\sigma=4$	
	Thermal Aging	1.6	23	5 Adhesive/Polyethylene Interface Failures
		$\sigma=0.4$	$\sigma=5$	
CL-50 Surface Flame Treatment	None	4.4	62	5 Adhesive/Polyethylene Interface Failures
		$\sigma=0.8$	$\sigma=12$	
	Thermal Aging	3.5	50	5 Adhesive/Polyethylene Interface Failures
		$\sigma=0.7$	$\sigma=9$	
Nylon 12	None	5.0	71	5 Adhesive/Nylon Interface Failures
		$\sigma=0.81$	$\sigma=11$	
	Thermal Aging	5.1	72	5 Adhesive/Nylon Interface Failures
		$\sigma=1.0$	$\sigma=14$	
Ethyl Cellulose	None	7.0	100	1 Adhesive Failure 4 Adhesive/Ethyl Cellulose Interface Failures
		$\sigma=3.2$	$\sigma=45$	
	Thermal Aging	7.9	112	5 Adhesive/Ethyl Cellulose Interface Failures
		$\sigma=2.4$	$\sigma=34$	

* σ $\bar{d}$ Standard deviation

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The standard deviations reported for the bond strength measurements are somewhat large. This, although unfortunate, was expected due to the excessive curvature of the candidate beaker materials as received. The material was obtained by slicing up already existing beakers. Hot pressing or ironing of the cut beakers and plates to improve their "flatness" was attempted with minimal success. These materials were therefore tested in their as received condition.

The results of Tables 9 and 10 indicate that Chemlok 305 and the DDI cure of R-45M adhesive both form an adhesive bond with all of the candidate beaker materials before thermal aging. Also, regardless of the adhesive used, the lowest and highest bond strength measured were obtained for the untreated polyethylene (CL-50) and ethyl cellulose respectively. This result is consistent with the degree of relative polarity of these materials as shown in Table 3.

The failure mechanism for the two adhesives were found to be quite different. Before and after thermal aging, all of the epoxy bonded joints failed via a brittle fracture with the majority of failures occurring at the adhesive/polymer interface. The exception to this behavior was the ethyl cellulose/epoxy joints which failed via three different mechanisms, cohesive failure of the ethyl cellulose, cohesive failure of the epoxy adhesive and adhesive failure at the ethyl cellulose/adhesive interface. It was very difficult to determine the exact makeup of the fracture surfaces in these particular joints after testing due to the greatly distorted fracture surfaces, hence the reported failure modes are the author's observations.

In an attempt to clarify this behavior, the maximum tensile stress (defined as the tensile stress at the time of joint failure) on the polymeric materials was calculated. For an adhesive joint bond strength of 54.4 Kg/cm² (Table 9), the resultant tensile stress on a specimen of ethyl cellulose of cross section 0.78 mm x 25 mm (typical dimensions of ethyl cellulose test strips) is 886 Kg/cm². The reported tensile strength of ethyl cellulose is 140 - 560 Kg/cm² [10]. Since these specimens were laminated to steel strips as an additional support to their structure these values of the tensile strength are somewhat higher, however, it is clear that the tensile stress during the measurement approaches the absolute tensile strength of ethyl cellulose and hence a cohesive failure of the test strips is quite possible.

¹⁰Gross, S. ed., "Modern Plastics Encyclopedia", 49(10A), McGraw-Hill, 1972, p. 146

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The fracture mechanism for all the urethane bonded adhesive joints differed before and after aging. Before thermal aging failure was via a tear-type separation with the adhesive being torn from the surface of all of the candidate polymers. This was somewhat expected since the adhesive is somewhat flexible. After thermal aging, however, failure was typically via a brittle fracture from the surface of the candidate polymers. This behavior is believed to be the result of additional curing during the thermal cycling process.

The effect of thermal aging on the measured bond strengths for the two adhesives was quite different. From the data of Table 10, it is concluded that the thermal aging cycle caused only a minor and relatively insignificant change in the adhesive bond strengths of each of the candidate beaker materials using the urethane adhesive. The effect on the epoxy bond strengths however was very significant, to the point where no measurable adhesion to untreated polyethylene (CL-50) and nylon 12 was present after thermal aging, Table 9. This significant weakening of the adhesive bond to surface flame treated polyethylene and the resultant debonding for nylon and untreated polyethylene are believed to be the result of two effects, namely, thermal expansion differences between the steel and polymeric test strips and possible embrittlement of the epoxy adhesive. It is believed, the cured epoxy being rather brittle before and after thermal aging could not accommodate the strain resulting from the differences in thermal expansion of the two joined adherends, and hence failed at the adhesive joint. The more strongly bonded polymer, ethyl cellulose, did not exhibit this behavior. After thermal aging, the adhesive bond to this particular material increased. This is believed to be the result of a post cure achieved during the aging cycle, and we conclude that the strain produced during thermal expansion was not sufficient to overcome this strong adhesive bond.

The above discussion points out the value of a more flexible adhesive like BDI cured R-45M in an application of this type, since from the data of Table 10, this adhesive appears to adequately accommodate the strain buildup caused by thermal expansion.

One final observation is apparent from the results of the adhesive bond strength measurement, the effect of flame treatment of polyethylene. The results show bond strength increases of two to three times the value for the untreated polymer. Also, the additional surface reactivity or polarity produced by flame treatment appears to be unaffected by the thermal aging process as is evident from a comparison of the results in Table 10.

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CONCLUSIONS AND RECOMMENDATIONS

The significant conclusions derived from the evaluation of the six candidate polymeric beaker materials are:

- 1) All candidate beaker materials are compatible with PBXN-106.
- 2) PBXN-106 cast into a clean beaker will adhere to the surface of the beaker. The strength of the resulting bond was found to be independent of the polymeric beaker material and unaffected by thermal aging.
- 3) Before thermal aging, the adhesive bond formed between the candidate beaker materials and primer coated steel using Chemlok 305 was significantly stronger than the DDI cured R-45M adhesive bonds.
- 4) Thermal aging significantly weakened the adhesive bond formed using the epoxy adhesive but had no significant effect on the adhesive bond formed using the urethane adhesive.
- 5) Surface flame treatment of polyethylene (CL-50) has a significant effect on the adhesive bonding ability of this material.

Based on the results and conclusions obtained in this study the recommended beaker material and adhesive for this service application are:

Beaker: fabricated from Phillips CL-50 polyethylene, the inside of which is untreated while the outside is surface flame treated.

Adhesive: Hexatriacontanediisocyanate (DDI) cured polybutadiene (ARCO's R-45M poly bd).