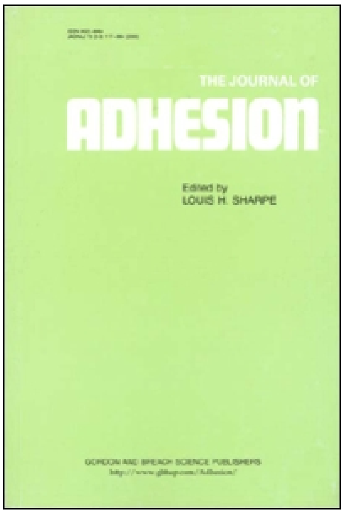

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Applied Research and Development of Adhesives for Bonding Filled Carboxyl Terminated Polybutadienes to Various Substrates

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A one-year applied research and development program was conducted on the bonding of carboxy-terminated polybutadiene (CTPB) propellant to various substrate materials encountered in solid propellant rocket motors. Under this program, in addition to CTPB liners, liners were also prepared from polyesters, polyethers, polyurethanes, polyacetal polymers, and epoxy resins. The use of various crosslinkers, emulsifiers, wetting agents, fillers, and stabilizers was also evaluated.

Four optimized liner formuations with the best all-round properties were fully characterized. The optimized formulations represented an HC liner formulation with two levels of glycerol additive, an HC formulation with a sorbitol additive, and a Butvar polyacetal-type liner. A standard HC-polymer liner formulation, designated as TL-H-304, was used as a control.

Unaged liner peel and shear properties were measured at −65°F, 77°F, and 160°F. Samples, aged for 30 days at 160°F, were tested at 77°F only.

The liners were tested against propellant, steel, aluminum, magnesium, titanium, epoxy-fiberglass, phenolics, polyisoprene, and butadiene-acrylonitrile as substrate materials. The steel, titanium, and polyisoprene rubber substrates gave the best adhesive results.

The substitution of asbestos and Cab-O-Sil for the Thermax filler in the liner gave comparable adhesive results while the substitution of clay fillers gave poor results.

This program was performed while at the Elkton Division of the Thiokol Chemical Corporation in fulfillment of the requirement of Contract N123 (60530-53329A) U.S. NAVAL ORDNANCE TEST STATION, China Lake, California, reported previously in U.S. Naval Report NOTS-TP4283.

† This paper was presented at the *Symposium on Recent Advances in Adhesion* during the 162nd National American Chemical Society Meeting, September, 1971.

INTRODUCTION

Future advances in the performance of either high speed military aircraft or sophisticated weapons systems can be expected to impose more stringent requirements on the performance capability of solid propellant rocket motors. As a result, the ability of such motors to repeatedly withstand both the low temperatures at flight altitudes and the elevated temperatures associated with high speed aerodynamic heat must continually be improved.

The potential for improvement in the performance capability of case-bonded solid propellant rocket motors depends strongly upon the behavior characteristics of the adhesives that are available to bond the propellant grain to the motor case and to other substrate materials. This results from the fact that such an adhesive (hereinafter referred to as a liner) must not only bond the propellant to substrate materials having different thermal coefficients of expansion, but also must successfully resist the degenerative effect of severe thermal gradients during the service life of the rocket motor unit.

Of the adhesive (liner) compositions now available for bonding carboxy-terminated polybutadiene (CTPB) propellants to various substrate materials in solid propellant rocket motors, none would appear to be completely satisfactory for future advanced applications.

To fulfill the program objectives, the overall approach under this investigation was subdivided into three general and somewhat overlapping phases.

1) *Phase 1* was concerned with the suitability of various chemical ingredients for use in the formulation of liner compositions. In this respect, a variety of chemicals were evaluated for their surface tension properties and for their effect in different formulations on shear and peel test results.

2) *Phase 2* was concerned with the definition and comparison of various liner formulation systems. Changes in the relative amounts of different ingredients and the substitution of one ingredient for another were evaluated with and without an inert filler component.

3) *Phase 3* was concerned with the selection, development, and evaluation of one or more liner compositions considered to be more attractive than those currently available for case-bonding CTPB propellants to rocket motor substrate materials.

A. MATERIALS EVALUATION

1. Surface Tension Studies

The purpose of these studies was to identify the various parameters which affect the work of adhesion, a theoretical measure of the interfacial bond strength between a material and its substrate. Since the work of adhesion is approximately equal to the product of the material's surface tension and the quantity ($1 + \cos \theta$), it was necessary to determine the values for surface tension and contact angle as a function of the parameter under study.

The experimental portion of this study was initiated by the determination of surface tension values for a variety of materials considered to be attractive for use as ingredients in liner formulations. The results show that surface tension values may vary quite significantly with the nature of the material being tested. Even when the materials are closely related, as the carboxyl-terminated polybutadiene (CTBX) and butadiene/acrylic acid copolymers (HA) are, the difference in surface tension values is as great as nine percent.

Concurrently, measurements were made on the surface tension of the standard liner, TL-H-304 (Table I), during the early stages of cure. The

TABLE I

Liner Composition

Ingredient	TL-H-304 (wt., %)	Equivalents
HC	73.62	0.0400
ERL-0500	2.33	0.0212
MAPO	2.05	0.0277
Iron Octoate	1.00	
Thermax	21.00	
	curing agent to polymer ratio $\frac{0.0489}{0.0400} = 1.23$	

results show that the surface tension of TL-H-304 changed drastically (over 100 percent) during the cure, thereby raising a question of the usefulness of further tension tests on ingredient materials or uncured liner compositions. Even if the surface tensions of uncured liners increase proportionally during cure, this would not account for the lack of correlation between the work of adhesion values and the shear specimen test values.

After experiments involving the addition of dispersing agents or solvents to the liners for effects on wetting, it was concluded that the surface tension and contact angle measurements, as run, did not and probably could not accurately represent either the true work of adhesion at an interface or the shear and peel properties of liner-substrate combinations.

2. Adhesion Studies

The purpose of these studies was to identify the various parameters which affect the magnitude and nature of liner-substrate shear test results. In keeping with this intent, a wide variety of ingredients was incorporated in liner compositions, different curing conditions were explored, and variations in substrate materials were briefly investigated.

In general, all of the candidate ingredients for liner compositions were initially evaluated on the basis of cup-cured gumstock samples. Those materials which yielded samples that were difficult to cure, or samples that were too brittle, or samples that qualitatively lacked good tear adhesion properties, were eliminated.

With the identification of these parametric effects on adhesion values, the work under Adhesion Studies and the work under the first phase of this investigation, Materials Evaluation, were effectively brought to a close.

B FORMULATION COMPARISONS

The purpose of this second phase of the overall investigation was to evaluate and compare more thoroughly the five general liner systems which, in previous studies, showed the most promise for case-bonding CTPB propellants in solid propellant rocket motors. These systems, taking their name from the nature of the major polymeric ingredient in the liner composition, were the CTPB, polyacetal, polyurethane, polyester, and polyether systems.

In general, the procedure for this work first involved the preparation of gumstock samples to define the range of compositions to be studied within each liner system. The curing agents and modifying agents used in each system were limited only to those which had shown promise in earlier studies.

Following this preliminary work with gumstock samples, liner compositions with a filler content were formulated for each of the five systems and tested for their ability to bond TP-H-3062 propellant to a steel substrate. The actual test employed was a steel-liner-propellant shear test.

From the liner systems evaluated the following were not continued for reasons listed:

(a) Polyether—poor strength
(b) Polyester—marginal strength and failures in the adhesive zone
(c) Polyurethanes—poor low temperature properties, mode of failure

1. CTPB Liner System

In general, the CTPB liner system gave steel-liner-propellant shear stress values averaging over 100 psi. Depending upon the specific liner composition involved, the test specimens failed in a variety of ways.

The inclusion of glycerol or sorbitol in the composition significantly improves the adhesive strength of the liner (Fig. 1). Presumably, the hydroxyl groups contained within these ingredients contribute both to the formation of primary bonds between the liner and propellant and to the formulation of additional secondary bonds between the liner and its steel substrate.

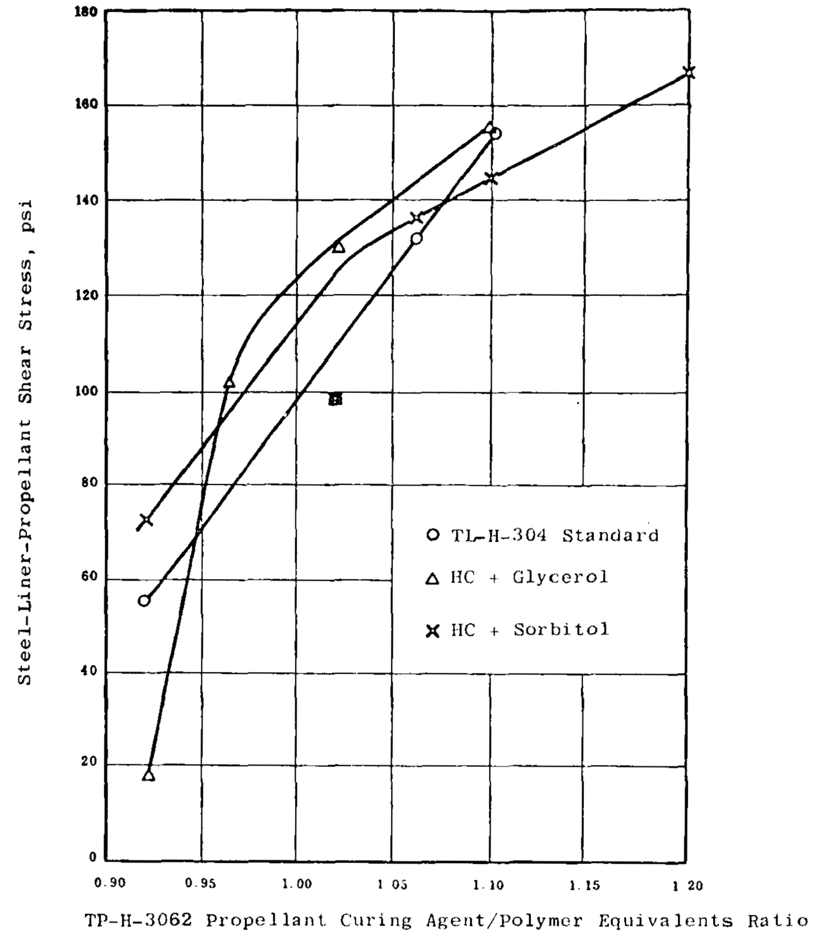

FIGURE 1 Effect of apparent propellant crosslink density on liner adhesion.

2. Polyacetal Liner Systems

Polyvinyl acetal resins are noted for their excellent adhesive characteristics on a variety of surfaces. Cures are easily effected by means of epoxides, phenolics, isocyanates, anhydrides, and melamines. The particular resin investigated was Butvar B-74 which is butyraldehyde based.

Preliminary work using Epon-1007 and ERL-2774-A with Butvar B-74 gave shear stress values of 119 and 153 psi, respectively. The specimen with ERL-2774 displayed propellant cohesive failure. Shear stress values over 150 psi having all propellant failures for maleic anhydride/epoxy mixed cures were also encountered. Maleic anhydride-epoxy mixed cure gave the best all-round adhesion properties obtained so far for the polyacetal system.

C. LINER CHARACTERIZATION

The purpose of this third phase of the investigation was to characterize the general adhesion properties of the four best liners resulting from all previous studies under this program. At the same time, a re-characterization of the TL-H-304 CTPB reference liner was to be conducted under the same conditions for comparative purposes.

The four best liners resulting from previous studies, along with the TL-H-304 reference liner, are shown in Table II.

TABLE II
Selected linear formulations and physical properties

Ingredient	Liner Composition (Parts by Weight)				
	A (Low Glycerol)	B (Sorbitol)	C (High Glycerol)	D (Butvar)	TL-H-304 (Standard)
HC	74.60	74.50	74.50	—	73.62
ERL-0500	—	—	—	13.50	2.33
ERL-0510	14.00	14.00	14.00	—	—
Glycerol	0.40	—	5.00	—	—
TEPA	0.03	0.04	0.04	—	—
Sorbo (solution of sorbital)	—	6.00	—	—	—
Thermax	11.00	11.00	11.00	11.00	21.00
Maleic Anhydride	—	—	—	1.45	—
Butvar B-98	—	—	—	17.50	—
MAPO	—	—	—	—	2.05
Physical Properties					
Stress, psi	237	168	267	—	288
Strain, in./in.	0.430	0.581	1.679	—	0.201
Modulus, psi	783	378	201	—	473

Liner A represents a carboxyl-terminated polybutadiene (HC) liner with a low amount (0.4 part) of glycerol additive. Liner C is also an HC liner with a higher concentration of glycerol (5.0 parts). Both of these compositions had good stress values (about 200 psi) and good strain values. Liner A has a strain of 0.43 in./in. and C had a 1.68 in./in. strain, reflecting the highet glycerol content. Liner B contained sorbitol and was satisfactory in physical properties, although by comparison it has lower stress (168) psi. The TL-H-304 composition also had satisfactory physical properties, although its strain of 0.20 in./in. is low.

The modulus of all the liners was satisfactory. No properties were run with liner D because it is more plastic in nature.

The effect of the crosslink density of the polymer in the propellant on the metal-liner-propellant shear properties is shown in Fig. 1. An increase in curing agent to polymer ratio (polymer in the propellant) of the propellant strengthens the liner to propellant bond and leads to higher shear strengths.

1. Unaged Liner Adhesion Properties

a. *Adhesion at 77°F.* The four liner-to-metal peel and shear properties were all at least twice as high as the standard, the Butvar liner being the highest in both cases and not even breaking in the shear test. (Figures 2 and 3). The

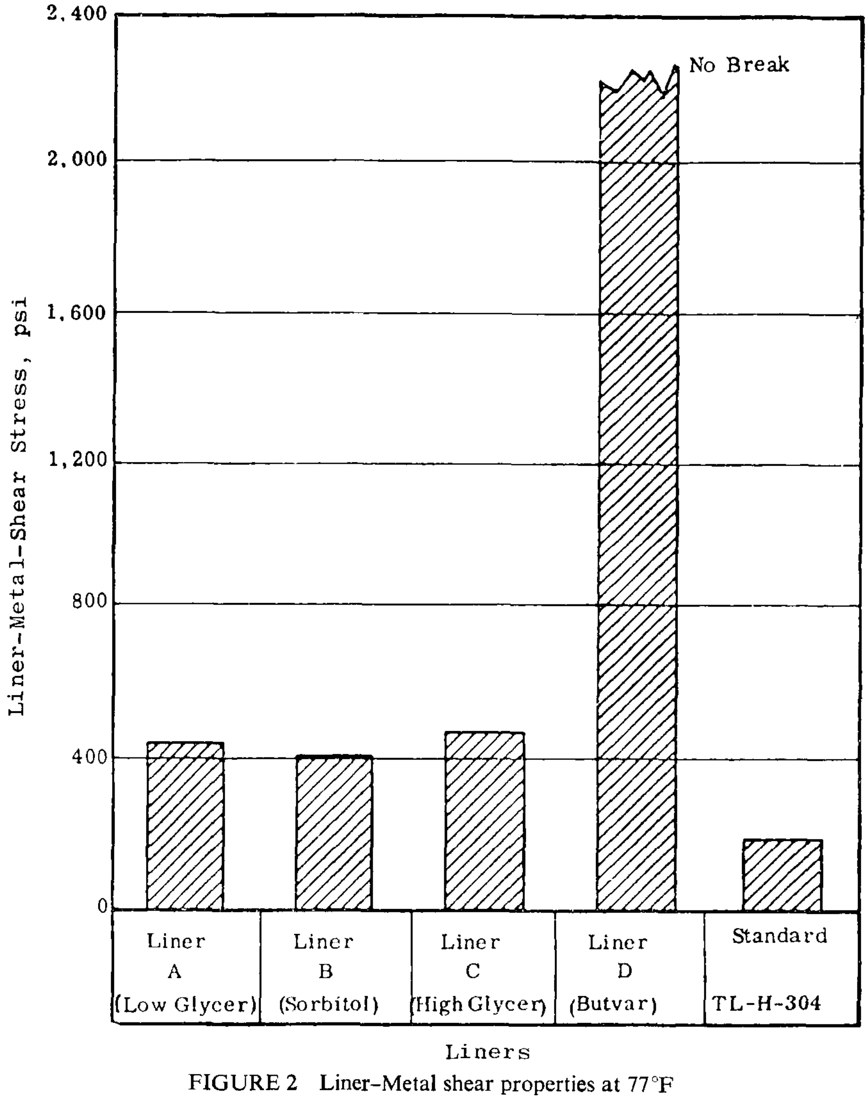

FIGURE 2 Liner-Metal shear properties at 77°F

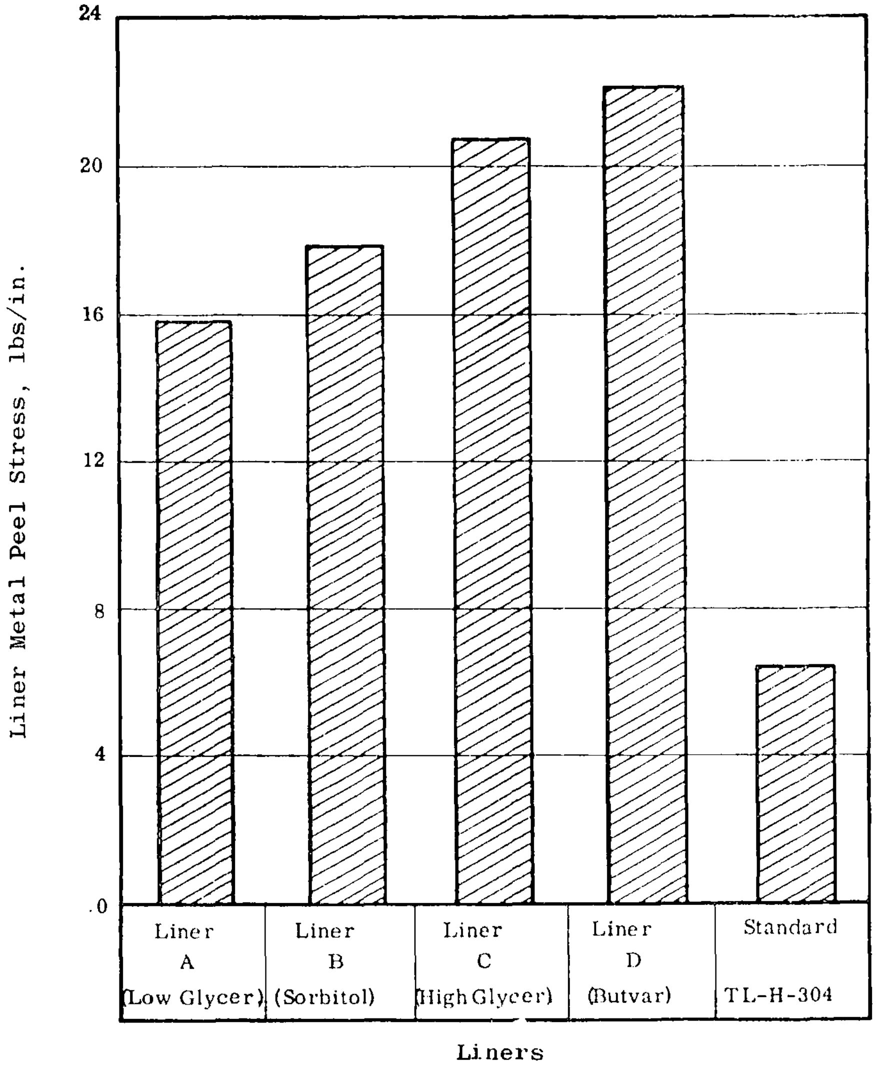

FIGURE 3 Liner–Metal peel properties at 77°F

metal-liner-propellant peel tests showed the glycerine-containing liners to be far better than the other three. The types of failure indicate that the presence of the polyhydroxy compounds strengthens the liner to propellant bond. The metal-liner-propellant shear tests show all four liners to have higher values than the standard TL-H-304 with the Butvar and low glycerine liner being 59 and 39 percent better, respectively. (Figures 4 and 5).

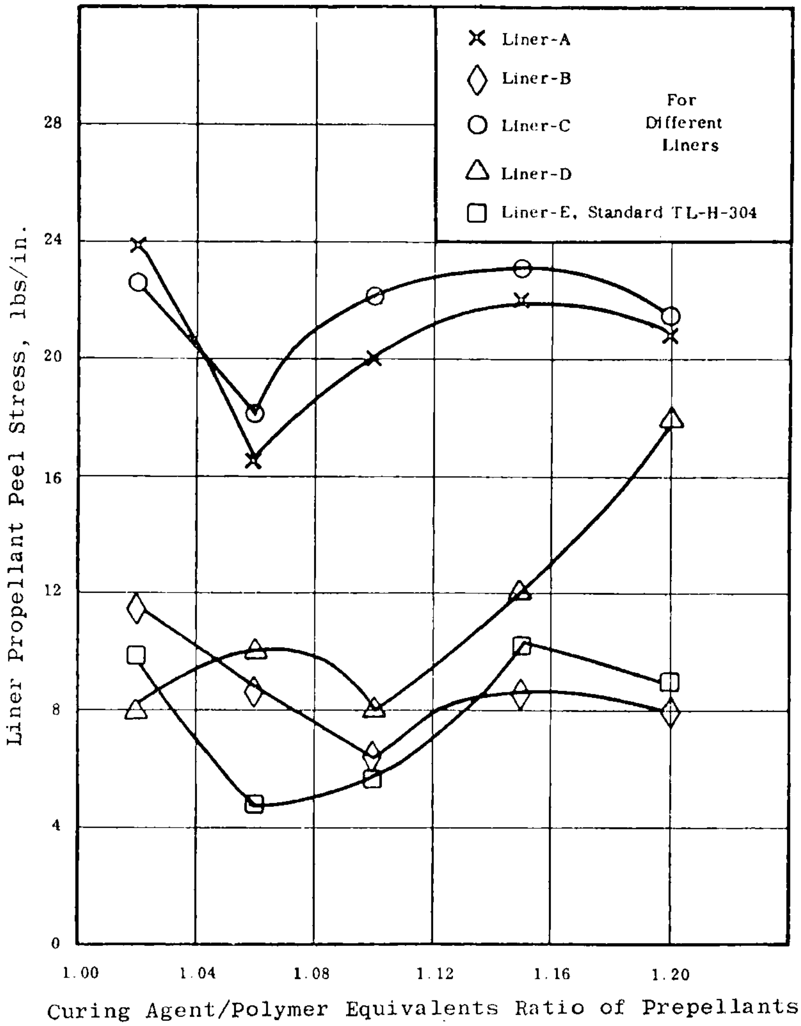

FIGURE 4 Liner-Propellant peel stress versus cure ratio of propellant at 77°F

b. *Adhesion at −65°F.* Except for the Butvar liner both the liner-metal peel and shear values were higher at −65°F than at ambient. The high glycerine liner had both the highest peel and shear value (Figure 6), indicating, perhaps, that glycerine is acting like a plasticizer at −65°F. The metal-liner-propellant peel values were comparable to these at ambient temperature and all were about the same value except the Butvar liner which had only 40% of this value (Figure 7).

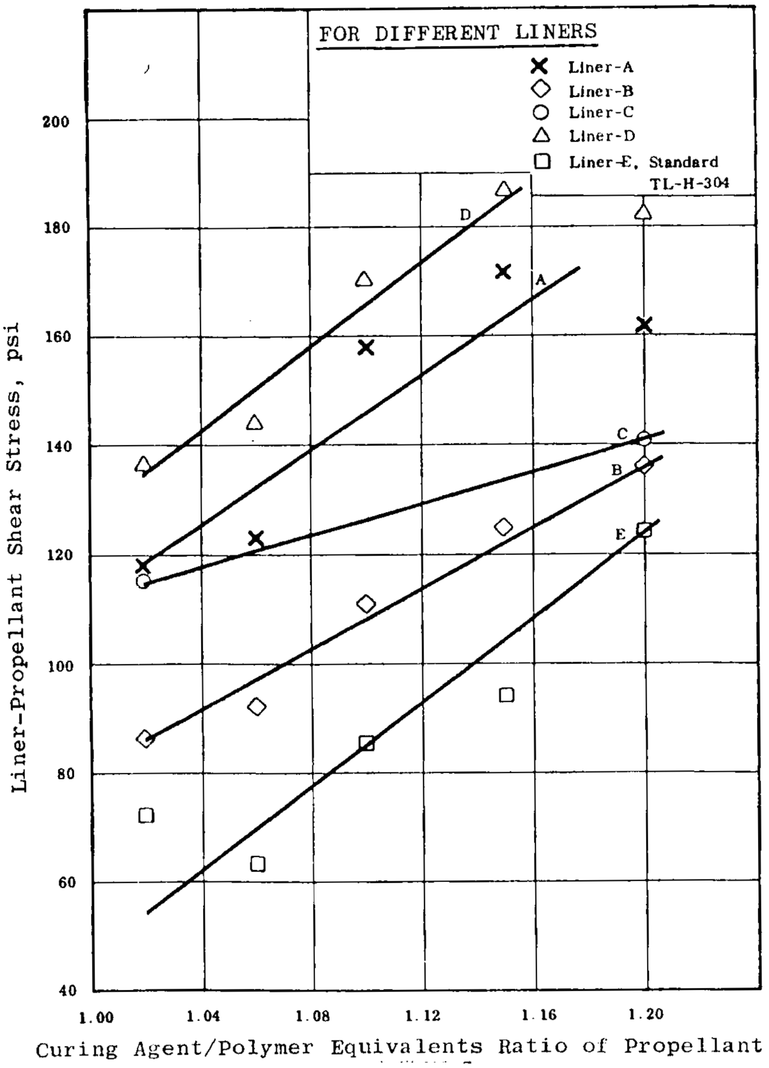

FIGURE 5 Liner–Propellant shear stress versus cure ratio of propellant at 77°F

c. *Adhesion at* 170°*F.* The metal-liner peel values were all poorer at 170°F than the corresponding values at ambient. The metal-liner shear values were all higher at 170°F than at 77°F (Figure 8). Without exception, the metal-liner-propellant properties were all lower than those at 77°F (Figure 9). The reason possibly for the lower adhesion values at 170°F than at 77°F is a decrease in the intermolecular forces at the higher temperatures.

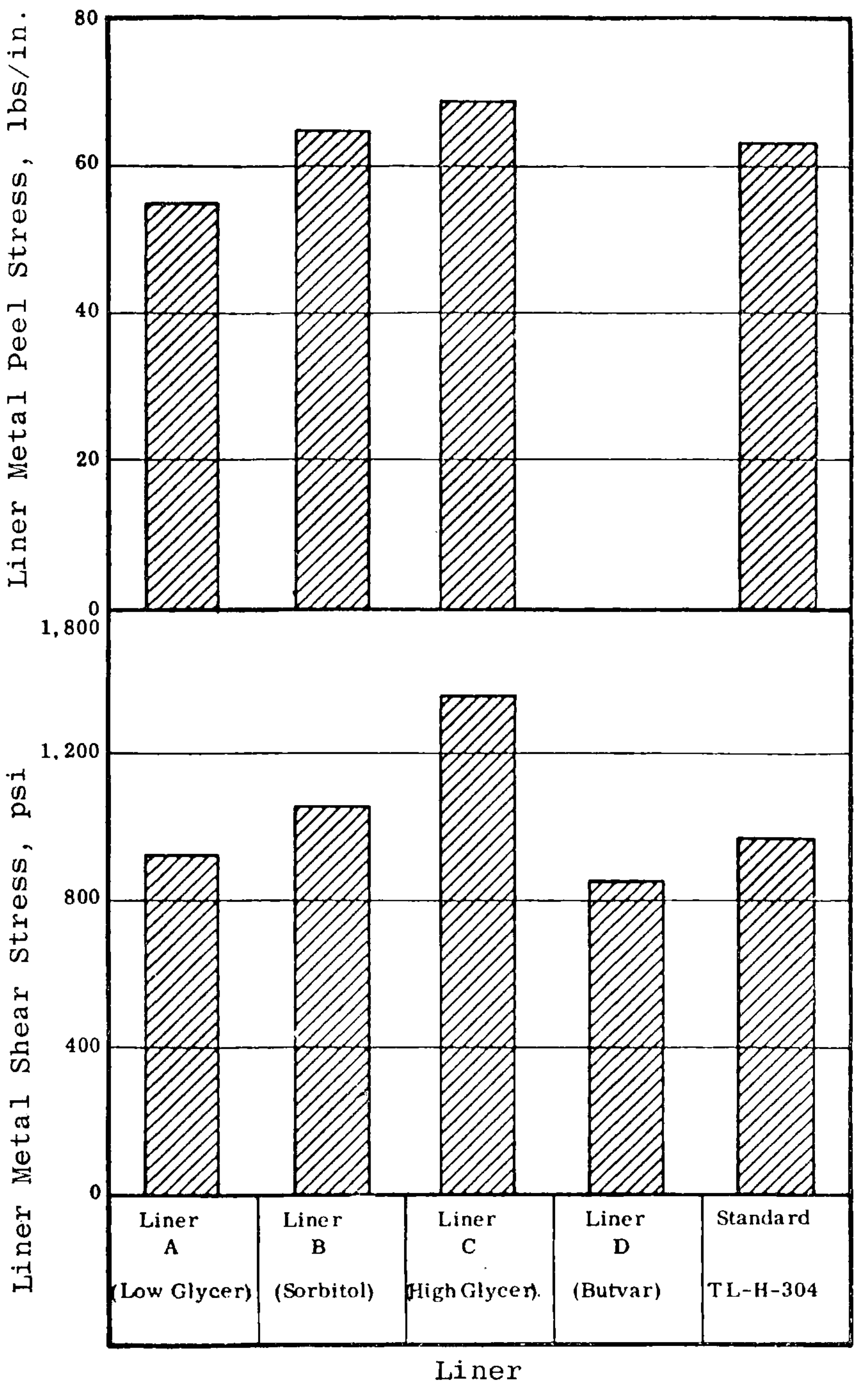

FIGURE 6 Liner-Metal properties at −65°F

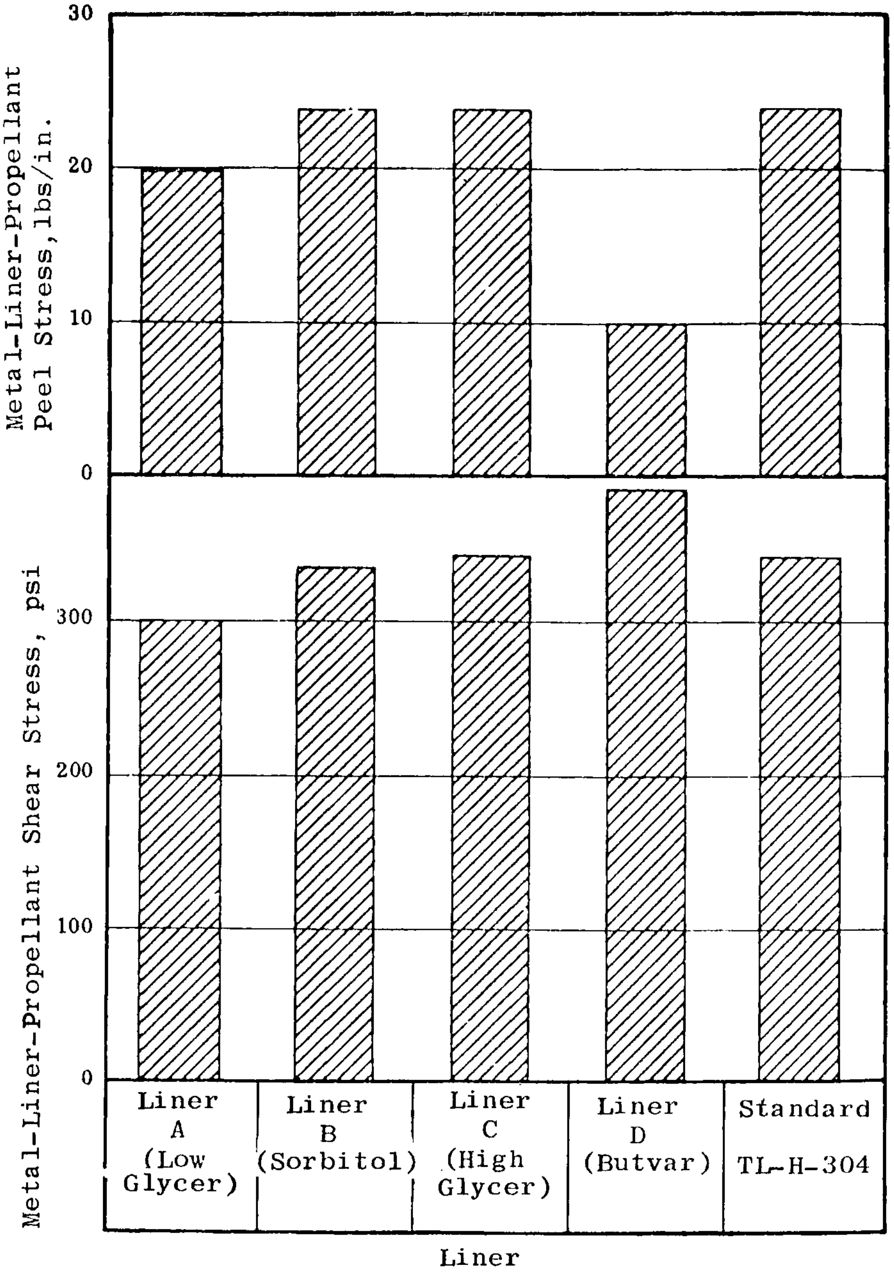

FIGURE 7 Liner propellant properties at −65°F

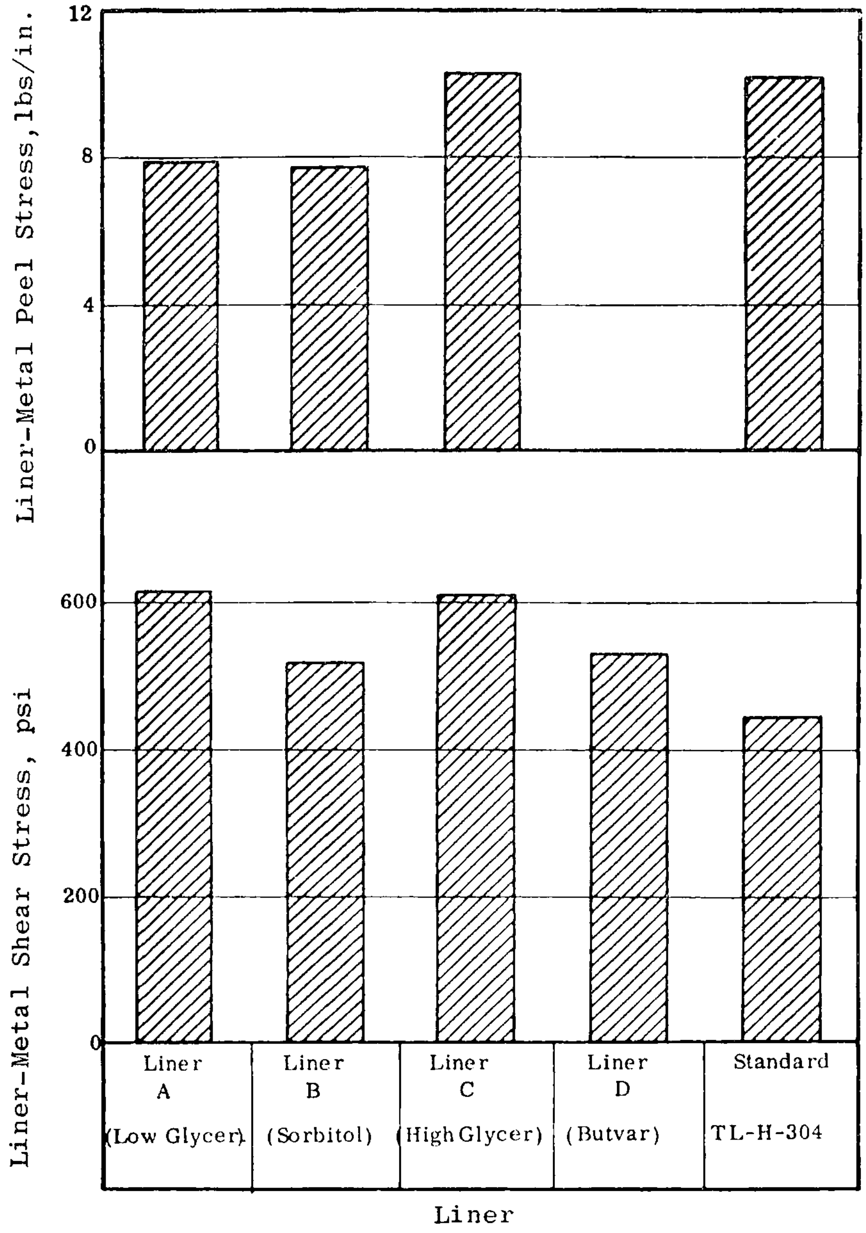

FIGURE 8 Liner–Metal properties at 170°F

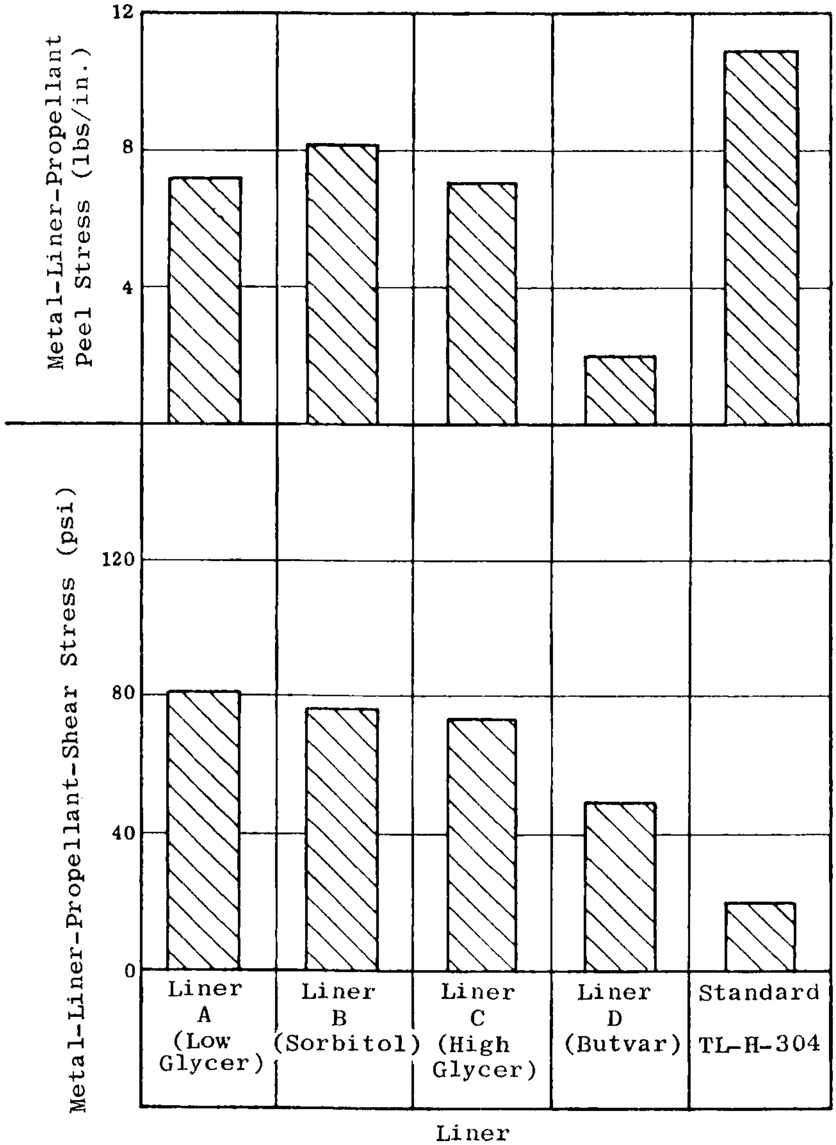

FIGURE 9 Metal-Liner propellant properties at 170°F

2. Aged Liner Adhesion Properties

Aging studies were conducted for thirty days at +160°F. Liner-metal and liner-metal propellant shear and peel tests were prepared and, after aging, were tested at 77°F.

a. *Liner-metal adhesion* Liner-metal shear values for the low glycerol liner, sorbitol liner, and Butvar liner underwent little change after thirty days aging. The standard TL-H-304 decreased slightly while the high glycerol liner aged very poorly. The liner-metal peel decreased in value except for the TL-H-304, which increased. The latter fact may indicate that the TL-H-304 liner may have insufficient state of cure. The high glycerol liner again aged

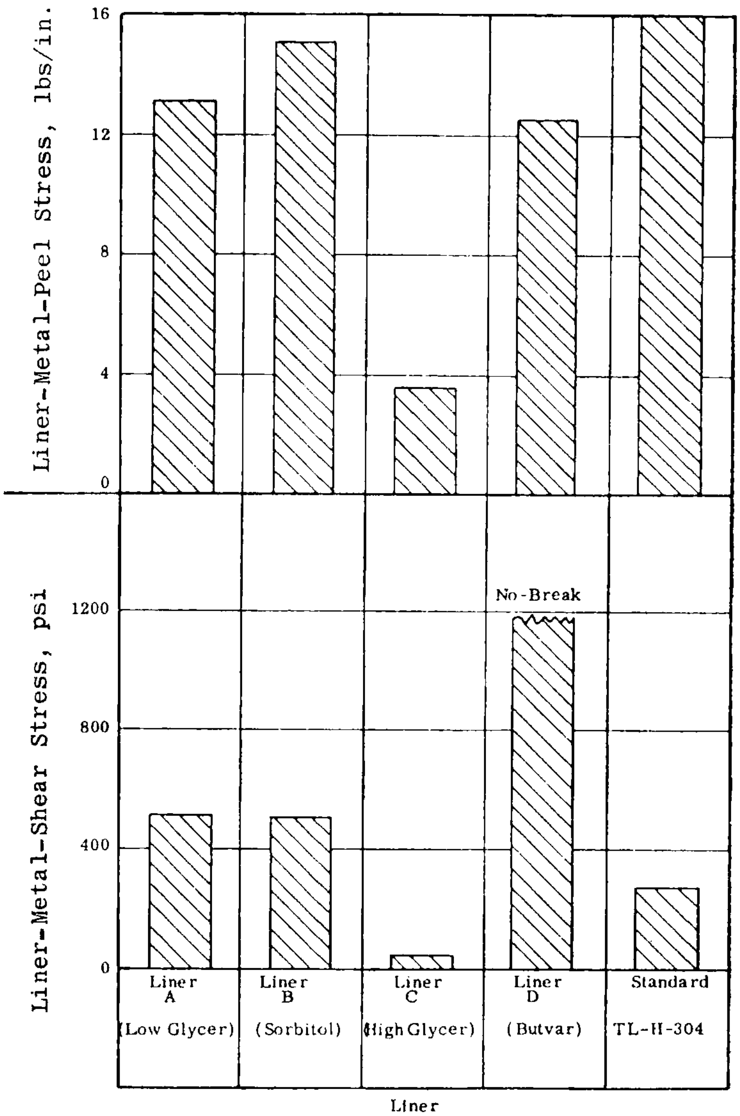

FIGURE 10 Liner–Metal properties at 77°F after one-month aging at +160°F

the poorest and had the poorest values. The poor aging probably results from the excess glycerol content which helps to plasticize the polymer to a very high degree and acts as release at the metal interface. The metal-to-liner data are shown in Figure 10.

b. *Metal-liner propellant properties* The metal-liner-propellant peel values after the thirty-day aging were all below ten pounds/inch indicating a marked decrease. The interfacial forces which are responsible for peel strength are evidently reduced in strength, especially the hydrogen bonding. Metal-liner-propellant shear has been chosen as the main criterion for screening the aging results. The propellant shear values are more reproducible than the comparable peel values. The Butvar acetal which aged the best retained 92 percent of its shear values, while the low glycerol liner retained 82 percent of its value, the high glycerol 67 percent of its value, and the standard TL-H-304 only 49 percent of its value. These data are shown in Figure 11.

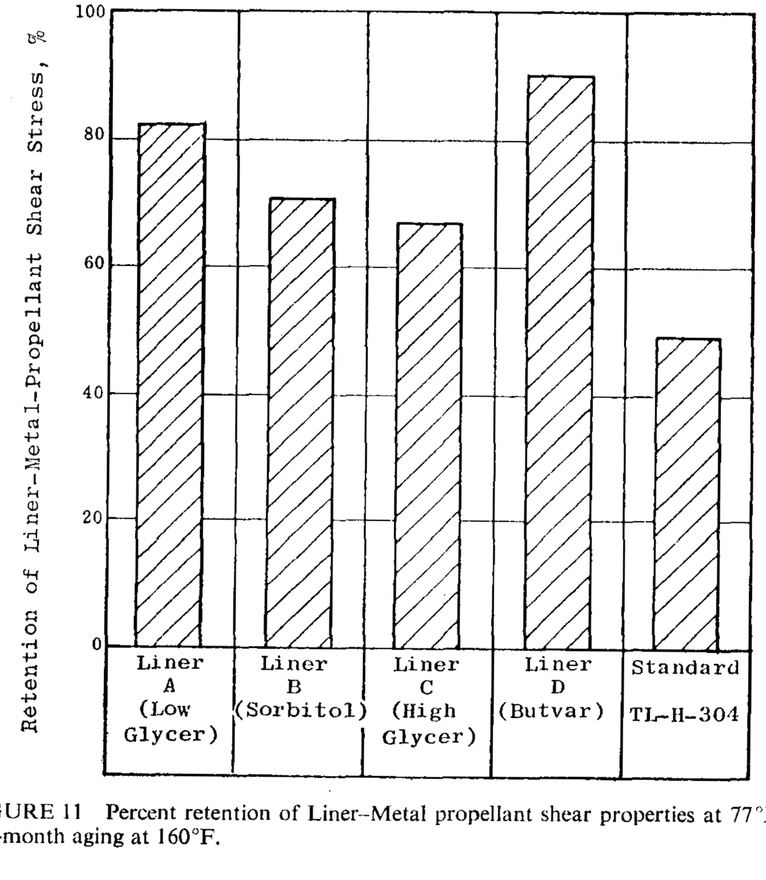

FIGURE 11 Percent retention of Liner–Metal propellant shear properties at 77°F after one-month aging at 160°F.

3. Filler Effects

Studies were made to replace Thermax as a filler for liners. Attagel and LVM Attapulgus clays, Cab-O-Sil, and asbestos were the fillers evaluated.

From the results of the liner-to-metal and metal-liner-propellant shear values, the following conclusions can be drawn.

a. *Liner-metal-shear* The liner-metal shear values for the asbestos floats were superior to, the Cab-O-Sil and Attagel clay values were comparable to, and the LVM clays were lower than those of the Thermax liner.

b. *Metal-liner-propellant shear* The asbestos floats and Cab-O-Sil filled liners had metal-liner-propellant shear values comparable to the Thermax liner while the liners containing Attagel and LVM clays had considerably lower values.

4. Substrate Effects

In the fabrication of solid rocket engines, numerous substrates other than steel are encountered. Therefore, in addition to steel, aluminum, magnesium, and titanium were evaluated. Plastics, such as epoxy-fiberglass and phenolics, and elastomers, such as polyisoprene and butadiene acrylonitrile, were also tested. A list of substrates with the code and/or type designation follows:

Substrate Type	*Representative Materials*
Metals	
Aluminum	7075
Magnesium	22-M-31-Comp. XK-60A-I-5
Steel	4130
Titanium	PI-6AL-4V
Plastomers	
Asbestos-filled polyisoprene	Garlock 531
Asbestos-filled NBR (plasticized)	Gen Gard V-44
Asbestos-filled NBR (plasticized)	Gen Gard V-50
Asbestos Phenolic (Raybestos)	RPD-150

The following results and conclusions were drawn from general observations and from the data.

a. *Metal substrate* Steel and titanium gave good metal-liner-propellant shear adhesion values; on the other hand, magnesium substrate resulted in average values and aluminum gave very low values. Eliminating the propellant from the adhesion samples resulted in satisfactory liner-metal shear and peel values for aluminum. The high and low glycerol content liners (C and A) gave higher shear values than the standard liner (E) for titanium and magnesium.

b. *Elastomeric Substrates* For the elastomeric substrates, both liner-metal and metal-liner-propellant shear tests were conducted. The results of these show that the polyisoprene 531 rubber contained no plasticizer and the V-44 and V-50 did. The shear values for the 531 rubber were average, while those for the V-44 and V-50 were considerably poorer.

c. *Plastic substrates* A similar situation to that of the elastomeric substrate exists for the tests made with phenolic and epoxy. When both liner-metal peel and shear and metal-liner propellant peel and shear tests were performed, very good liner-metal properties were obtained, but the metal-liner propellant results were poor.

CONCLUSIONS

1. The HC liners with low glycerine content had the best all-around adhesion properties based on the temperature and aging data.
2. The Butvar liner and the glycerine-containing liners gave the best shear values. The peel values of the glycerine-containing liners were superior to the others.
3. The addition of glycerine improves the adhesion of HC liners to different substrates and HC propellant. Other polyhydroxy compounds also improve the adhesion, but the steric factors of some of the molecules reduce their effectiveness.

GLOSSARY

Butvar B-74	Polyvinyl Butyral; Monsanto; M.W. = 100,000 - 1500
Butvar B-98	Polyvinyl Butyral; Monsanto; M.W. = 30 - 34,000
CAB-O-SIL	Finely divided silica
Epon 1007	Difunctional epoxy; Shell Chem. Co.; Eq. wt. = 2000 - 2500
ERL-0500 ERL-0510	Trifunctional epoxide; Union Carbide; Eq. wt. = 104–114 for 0500, 97–100 for 0510
ERL-2774	Difunctional epoxy; Union Carbide; Eq. wt. = 180–195
Hydrocarbon Polymers	
HA	American Synthetic, Polybutadiene-acrylic acid copolymer; Eq. wt. = 1560

HC	Thiokol Chem. Co.; carboxyl terminated polybutadiene; Eq. wt. = 1630 - 2000
CTPB	General term for carboxyl terminated polybutadiene
CTBX	Goodrich Rubber Co.; carboxyl terminated polybutadiene; Estimated Eq. wt. = 1400 - 2200

Compositional analyses of carboxyl terminated polybutadienes available are:

	% Vinyl	% Cis	% Trans	Functionality	Eq. wt.	Mol. wt.
HC (Thiokol, lot 30M)	30	22	49	2.1	1840	3950
HYCAR, lot -13 (B. F. Goodrich)	30	19	48	2.1	2090	4410

MAPO	Interchemical Corp., trifunctional imine, Eq. wt. = 73 - 75
TEPA	Tetraethylene pentamine
Thermax	Medium Thermal Carbon Black; R. T. Vanderbilt Co.