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Case Bond Liner Systems for Solid Rocket Motors

Prepared by

T. W. Giants
Materials Sciences Laboratory
Laboratory Operations

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SPACE SYSTEMS DIVISION
AIR FORCE SYSTEMS COMMAND
Los Angeles Air Force Base
P. O. Box 92960
Los Angeles, CA 90009-2960

Engineering and Technology Group

THE AEROSPACE CORPORATION
El Segundo, California

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Paul M Propp

PAUL M. PROPP, GM-14
MOIE Project Officer
SSD/WL/ML

JONATHAN M. EMMES, Maj, USAF
MOIE Program Manager
PL/WCO OL-AH

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The construction of a case bond liner system for solid rocket motors involves a series of processes designed to satisfy a variety of launch vehicle parameters. An attempt to understand the chemistry and processing variables and how they affect the interfacial bonding properties in barrier liner propellant formulations is presented. Interdiffusion rates and the rate of cure of each of the layers must be considered together to minimize changes in cure stoichiometries in the interfacial zones. The control of barrier layer cure is essential, not only to reduce migration of reactants and plasticizer from liner and propellant, but also to provide an active surface for adhesion to the liner. The importance of the proper characterization of the hydroxyl-terminated polybutadiene binder should not be underestimated. Because the binder material is a constituent of both the liner and the propellant, variation in cure times can impact diffusion rates. The complexity of case bond liner systems has increased over time, and with it, the number of variables. As more than one variable operates near its specification limit, the potential for failure becomes statistically significant. It is

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recommended that, in the present system, studies be directed toward refining the process variables further with the goal of increasing the reliability of bonds at all interfaces between layers.

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FIGURES

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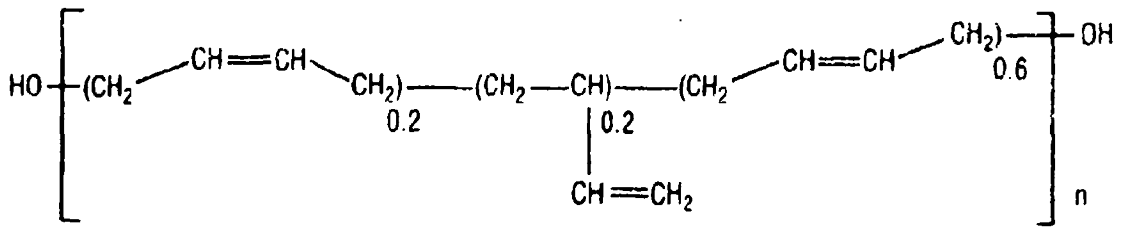
I. INTRODUCTION

Case bond liner systems for solid rocket motors have been formulated in a number of ways to maximize their design properties when interfaced with a propellant. Since a successful case bond liner system is one that fails cohesively in the propellant, any other mode of failure in the system is unacceptable. The chemistry of the system is quite complex, and an attempt is made in this report to describe the delicate role of each process in constructing a case bond and the limitations inherent in these processes.

II. BACKGROUND

Binders for composite solid propellants are chosen for particular property requirements. The major requirement is to obtain the optimum specific impulse from a composition of the binder, which is a hydroxy-terminated polybutadiene (HTPB) and a diisocyanate curing agent, in combination with ammonium perchlorate and aluminum. This binder system has been extensively investigated to elucidate factors influencing mechanical behavior and to establish the failure criteria of solid composite propellants. The ideal binder is chosen to maximize the propellant content, have a high fuel value, and exhibit specific mechanical properties after cure.

HTPBs combine the high fuel value of hydrocarbons with the good mechanical properties of polymers cured through terminal functional groups. These HTPB prepolymers are used as fuel binders to yield a variety of propellant compositions when cured with various diisocyanate compounds. The use of the HTPBs permits the formulation of composite propellants of very high specific impulse by optimizing the ratios of the organic binder, the ammonium perchlorate oxidizer, and the aluminum metal. Since these propellants are formulated with a very high volumetric loading of oxidizer and metal powder, great reliance is placed on the binder to obtain the best mechanical properties (Ref. 1). Because side reactions occur during cure of this binder system, stringent control during processing of the propellants is required to ensure reproducible mechanical properties. The use of HTPBs as propellant binders has been treated extensively in the literature. The chemical structure of the HTPB resin, commercially available as R-45M, is depicted in Figure 1.



n ≈ 50

MICROSTRUCTURE (all polymers):

TRANS-1,4 UNSATURATION	60%
CIS-1,4 UNSATURATION	20%
VINYL-1,2 UNSATURATION	20%

Figure 1. Structure of R-45M

Because of the method of manufacture and the nature of the HTPB molecule, it is susceptible to oxidation and must be stabilized to allow adequate shelf life. In the presence of oxygen and native peroxide contaminants, the HTPB can undergo a variety of reactions, as shown in Figure 2 (Ref. 2).

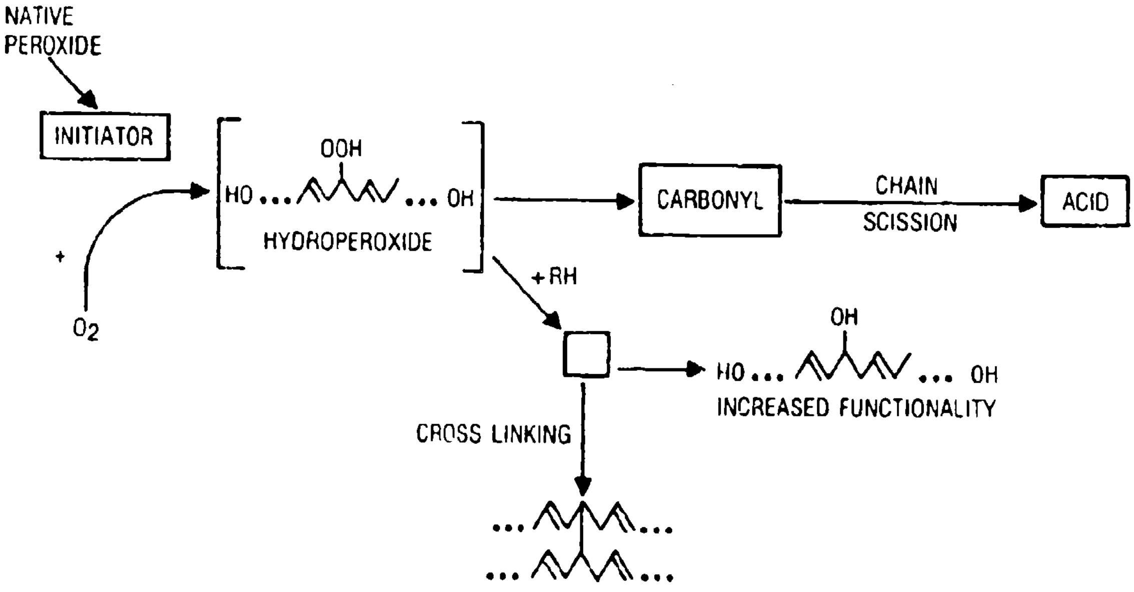
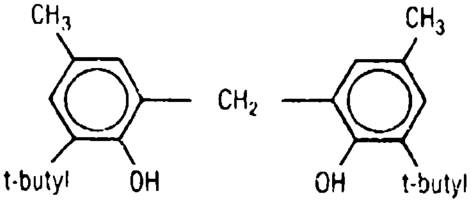


Figure 2. Chemical Behavior of HTPB (R-45M) to Oxidation

The generation of hydroperoxides leads to the formation of acids through chain scissioning and to cross-linking or increasing hydroxyl functionality through different mechanisms. Thus, antioxidants are added to reduce this susceptibility to oxidative degradation. In this instance, a hindered phenol, AO-2246, is used to stabilize the HTPB:



AO-2246

Figure 3 (Ref. 3) exhibits an experiment designed to show the effect of oxidation on HTPB after the inhibitor is depleted.

For an adequately stabilized HTPB, the only reaction taking place is the destruction of antioxidant, described as an induction period in Figure 3. After the antioxidant is consumed,

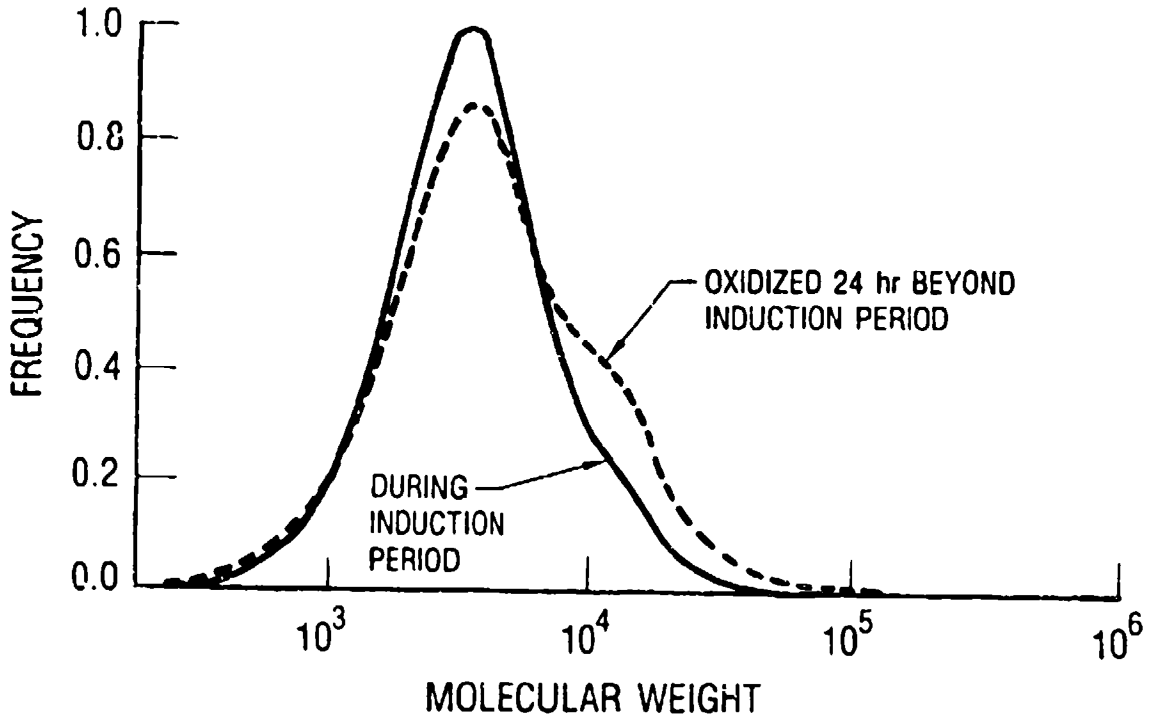


Figure 3. Effect of Oxidation on Molecular Weight Distribution of HTPB (R-45M)

rapid peroxide formation and polymerization take place. The change in molecular weight distribution reveals the effect of oxidation on HTPB. An increase in functionality leads to an increase in homopolymerization, resulting in increased viscosity and eventually increased cross-link density, all of which affect pot life and subsequent aging characteristics. Thus, it is important to stabilize the HTPB binder early in the production process while assuring that the antioxidant does not interfere with subsequent processes. Commercially available R-45M has an exceptionally low viscosity (50 ± 10 Ps @ 30°C), permitting processing of propellants with higher solid loadings. The functionality of R-45M (2.2–2.4 hydroxyl groups per molecule) permits cross-linking by readily available difunctional isocyanates. Ultimate propellant mechanical properties are directly related to the initial isocyanate/hydroxyl ratio (NCO/OH) (Ref. 4). In this particular formulation, the ratio is < 1 (~ 0.8). Sensitivity to this ratio is illustrated in Figure 4, where a specific propellant modulus is desired (Ref. 5).

In addition to the reactive components just described, the propellant formulation includes antioxidants to prevent the homopolymerization of the R-45M, an inert plasticizer to reduce the viscosity of the propellant system, and a bonding agent that enhances the oxidizer-to-binder bonding properties.

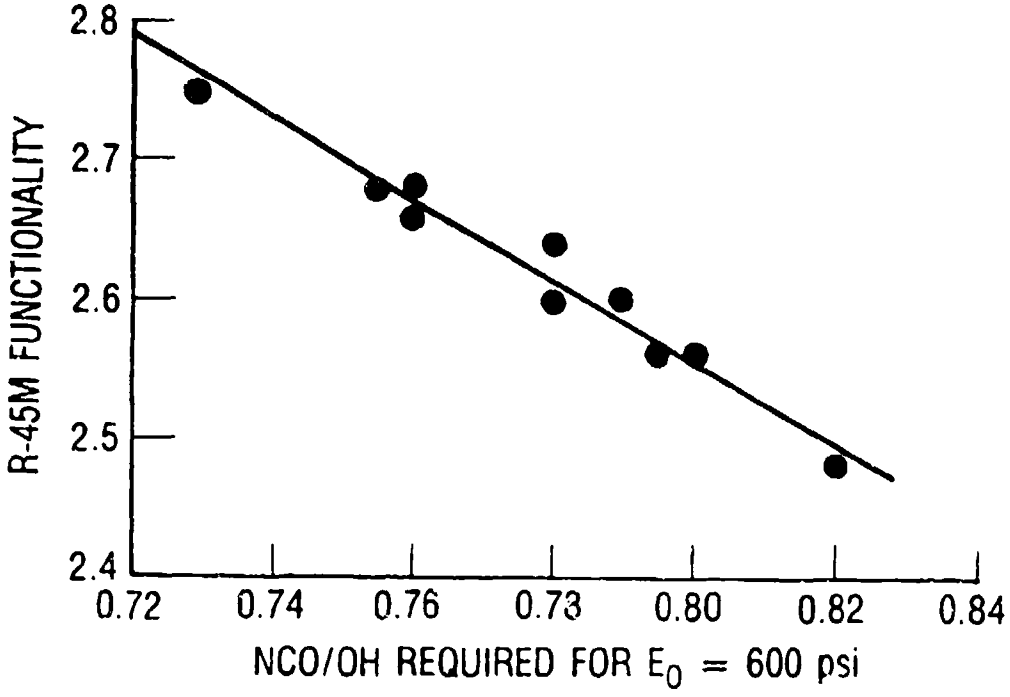


Figure 4. Correlation of R-45M Functionality with Propellant NCO/OH Requirement

The single most important contributor to problems in the case bond liner system is moisture. Since diisocyanates react with water, its presence can upset the stoichiometries used and thereby affect end-use properties.

With this background, one can attempt to follow the progression of events leading to the system currently under study.

III. DISCUSSION

The propellant formulation described in section II is designed to have a working life long enough to be cast many hours after the propellant is made. The propellant is then allowed to cure slowly to its ultimate properties.

Rocket motor casings are usually lined with an insulation layer, which is mainly a protection for the case. This layer is an ethylene-propylene-diene elastomer, more commonly called an EPDM rubber.

Originally, the propellant was cast into the EPDM-lined case. However, the slow-curing propellant enabled propellant components to migrate into the insulation, resulting in a soft layer at the interfacial region (Ref. 4). Subsequently, a liner system was developed for placement between the insulation and the propellant to prevent this migration from occurring.

This liner system appeared to be a combination of R-45M with a diisocyanate curing agent and a carbon filler for strength. This formulation used an excess of diisocyanate to R-45M and was designed to act as an adhesive between the insulation and the propellant. Further work revealed that the plasticizer component of the propellant composition migrated through this liner and even into the insulation. One solution to this problem was to incorporate the migrating species into the liner formulation to closely maintain an equilibrium condition at the surface while curing was taking place. This incorporation required a corresponding increase in the filler content to maintain the liner viscosity properties. Still, the liner insulator interface continued to show migration with deleterious effects on the liner chemistry (Ref. 6).

A subsequent approach described the application of a barrier coating to the insulator that would not pass any of the interacting components mentioned. This barrier coat would be sufficiently designed to inhibit any migration from the contacting liner, while at the same time providing a compatible surface for adhesion to the liner. The result of all this activity was a case bond liner system assembled in the following way (see Figure 5) (Ref. 7).

The case adhesive insulator system is prepared separately, and the insulator surface is cleaned and dried under thermal vacuum conditions to limit the accessibility of water to the moisture-sensitive layers yet to be applied. In the manufacturing operation, the subsequent layers are applied according to a predetermined set of specifications.

The chemistry of the accompanying steps is rather fascinating.

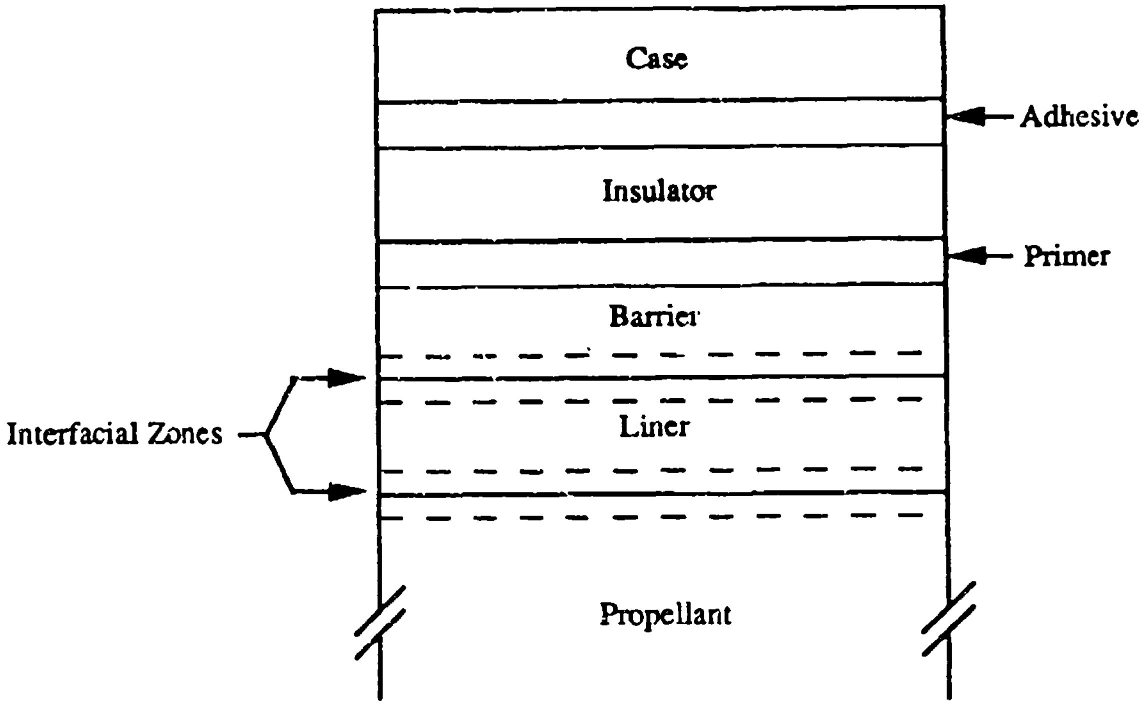


Figure 5. Schematic of Case Bond Liner Propellant System

The insulator surface is treated with a primer that is compatible with both the insulator material and the barrier material to provide good adhesion between those layers. The barrier coating is a polyurethane-based, tolylene diisocyanate-terminated prepolymer filled with titanium dioxide and is cured by ambient moisture. The barrier depends on the temperature and relative humidity conditions for optimum cure. A chart describing these conditions is shown in Figure 6.

As one can see, the temperature-humidity conditions are very important in attaining the proper cure.[*] When the barrier coating is "sufficiently" cured, the liner is applied. The liner consists of a mixture of HTPB, dimeryl diisocyanate (DDI) curing agent , dioctyl sebacate (DOS) plasticizer, carbon black filler, and an aziridine-based bonding agent, HX-868. This mixture is applied as a spray coating in 1,1,1-trichloroethane. The propellant is then cast into the motor casing.

Although this sequence of steps describes one common process for a propellant binder system, and each step by itself can be controlled, when taken together, the processing times

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[*] R. Bretzlaff and R. J. Sugihara, *Cure Kinetics of Chemglaze Z-451 Polyurethane with 9984 Co-reactive Catalyst*, ATM-89(4533-01)-22 The Aerospace Corp., El Segundo, CA (14 April 1989).

and temperatures for each layer can be crucial to the ultimate bonding properties at the interfaces between the layers.

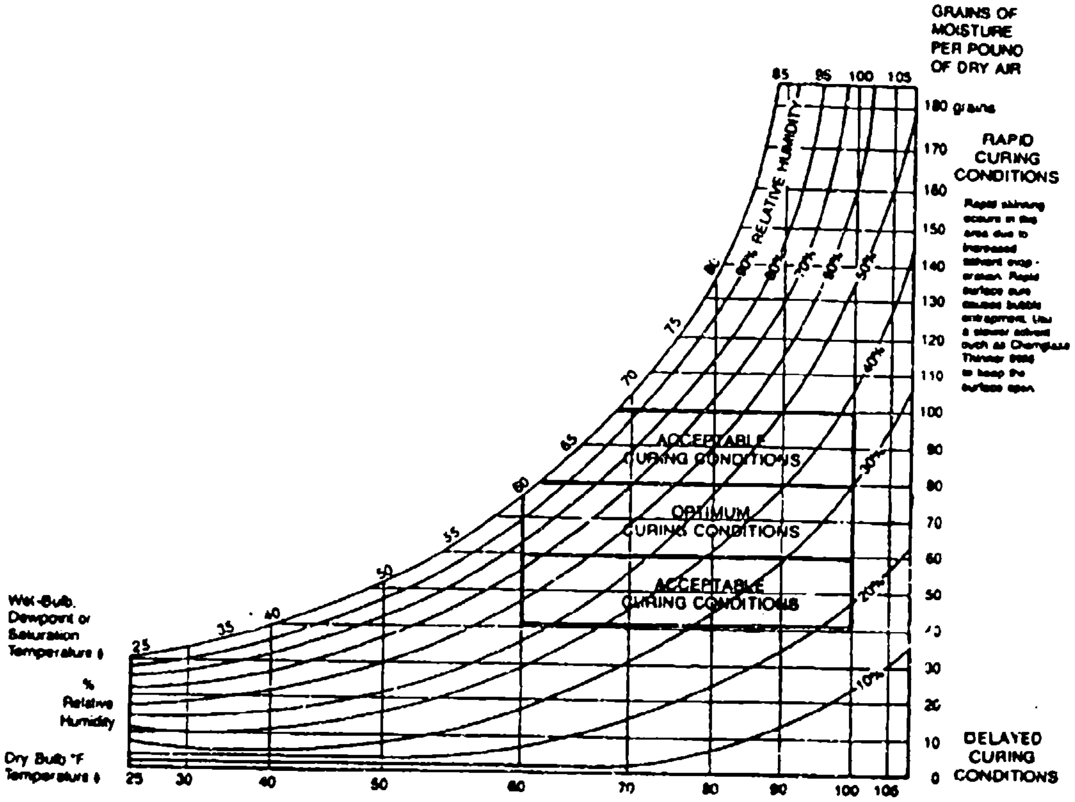


Figure 6. Psychrometric Chart Describing Curing Conditions for Barrier Coating (Lord Corporation)

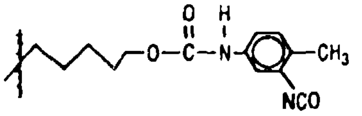
A case bond liner system is said to be successful if the failure mode occurs cohesively in the propellant. With this requirement in mind, one can appreciate the complexities associated with curing the individual layers to their desired cohesive properties while simultaneously forming good bonds at the interfaces. Since the insulator and propellant are specifically designed to maximize their properties of case protection and burn rate, respectively, the chemistry of the liner system used to properly mate these systems is of extreme importance.

In section IV, the focus will be on the interlayer and the conditions under which optimum properties are obtained.

IV. CHEMISTRY

The barrier layer is a commercial moisture-curing polyurethane containing titanium dioxide filler and an accelerator and is spray coated to a 1 mil thickness. This layer is then allowed to cure under ambient conditions from 1 h to 7 days (according to the manufacturer). Note that this material is formulated as an abrasion- and solvent-resistant topcoat when fully cured. Figure 6 displays the optimum conditions of cure for the intended purpose of this material. Curing proceeds by diffusion of ambient moisture into the layer, reacting with the tolylene diisocyanate-terminated prepolymer. If one wishes to apply multiple coats of this layer, it is important to do so within a very short time, since a cured layer becomes impenetrable even to an identical coating (see Table 1).

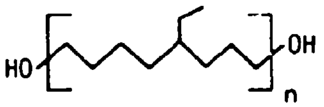
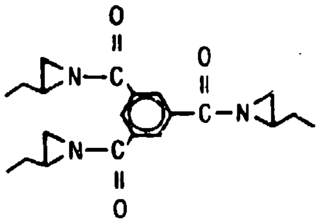
Table 1. Reactive Barrier Components

DESIGNATION	STRUCTURE
Z-451 (SEGMENT)	
MOISTURE	H_2O
CATALYST (9984)	$[CH_2N\text{-}(CH_2CHOH\ CH_3)_2]_2 + [CH_2N\text{-}(CH_2CHNH_2CH_3)_2]_2$

When the barrier layer is "sufficiently" cured, the liner is applied. The reacting species in the liner are the HTPB and an excess of DDI curing agent. The DDI curing agent differs from its predecessors in two important ways. First, it has a 36-carbon chain between isocyanate groups and thus is more moisture resistant and less likely to hydrolyze. Second, being a much larger molecule, it is less prone to diffuse out of the liner. The purpose of the plasticizer, DOS, in the liner formulation is to inhibit the diffusion of DOS from the propellant into the liner. Thus, an equilibrium condition is set up for the DOS at the propellant-liner interface so that the interfacial chemistry is not affected adversely (see Table 2).

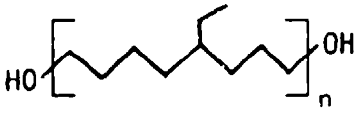
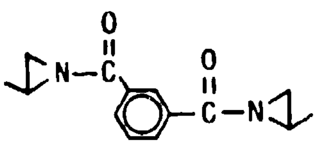
In addition to the components listed in Table 2, an aziridine bonding agent, HX-868, appears to have been added because of similar diffusion phenomena. The propellant formulation contains HX-752, a bonding agent of the same chemical family that is present to aid the bonding between the oxidizer (AP) and the binder (R-45M). Since diffusion is also possible

Table 2. Reactive Liner Components

DESIGNATION	STRUCTURE
HTPB	
DDI	$OCN\text{-}(CH_2)_{36}\text{-}NCO$
HX-868	

with this bonding agent, a similar rationale to that used for the plasticizer problem appears to have been employed (see Table 3).

Table 3. Reactive Binder Components

DESIGNATION	STRUCTURE
HTPB	
DDI	$OCN\text{-}(CH_2)_{36}\text{-}NCO$
HX-752	

One can appreciate, because of a necessarily slow propellant cure rate, that the interdiffusion rates at the various layer interfaces are extremely important to the chemistry of the liner in the formation of adequate adhesive bonds.

The barrier chemistry results in the formation of a polymer derivative from the reaction of Z-451 with water. This is a slow reaction requiring an accelerator and is dependent on the diffusion of ambient moisture (see Table 1.)

Since interdiffusion is thought to play an important role in the adhesion of the liner to the barrier, allowing the barrier to cure completely would inhibit this interdiffusion and reduce interfacial bonding.

The liner formulation uses an isocyanate-to-hydroxyl ratio (NCO/OH) greater than 1 partly to compensate for nascent moisture present. However, more important, this ratio allows access of R-45M propellant binder to the unreacted isocyanate groups, thus increasing the bonding properties at this interface (see Table 2). Therefore, liner cure at these ratios should not be allowed to proceed to the point where cross-linking in the liner interferes with interdiffusion by the propellant binder components.

The propellant binder formulation described previously uses an isocyanate-to-hydroxyl ratio (NCO/OH) less than 1 to satisfy propellant mechanical properties. The remaining reactive component of the propellant is the bonding agent HX-752. This agent is one of a class of multifunctional aziridine compounds originally used as cross-linking agents in carboxyl-terminated polybutadiene (CTPB) propellant systems. Currently, these compounds are used in highly filled HTPB propellants to prevent blanching. Although the chemistry is not well understood, HX-752 apparently interacts with the ammonium perchlorate oxidizer, permitting better molecular association between the HTPB and the filler particles, and eliminates the void formation that can occur in its absence. Recently, evidence for the interaction of AP with HX-752 was shown by infrared spectrometry (Figure 7) (Ref. 8).

In Figure 7, one can easily observe that the spectra of AP and HX-752 are not simply additive but include new absorption peaks. This is probably due to homopolymerization of the HX-752 as the result of an acid-catalyzed ring opening of the aziridine system from residual moisture content in the AP. (About 0.002% water is present on the surface of AP crystals—ten times as much as in the internal structure).

In Table 2, the presence of HX-868 appears to serve two purposes: to help control the dynamics of migration of HX-752 and to participate in the surface reaction with the oxidizer particles. HX-752 and HX-868 react through ring-opening homopolymerization, which would also assist in the interfacial bonding between the propellant and the liner (see Reference 7, p. 75).

As one can observe by analyzing the formulation of the propellant liner insulator system, the liner surface chemistry is very complex, and a great deal of attention must be paid to the processes by which these layers are brought together.

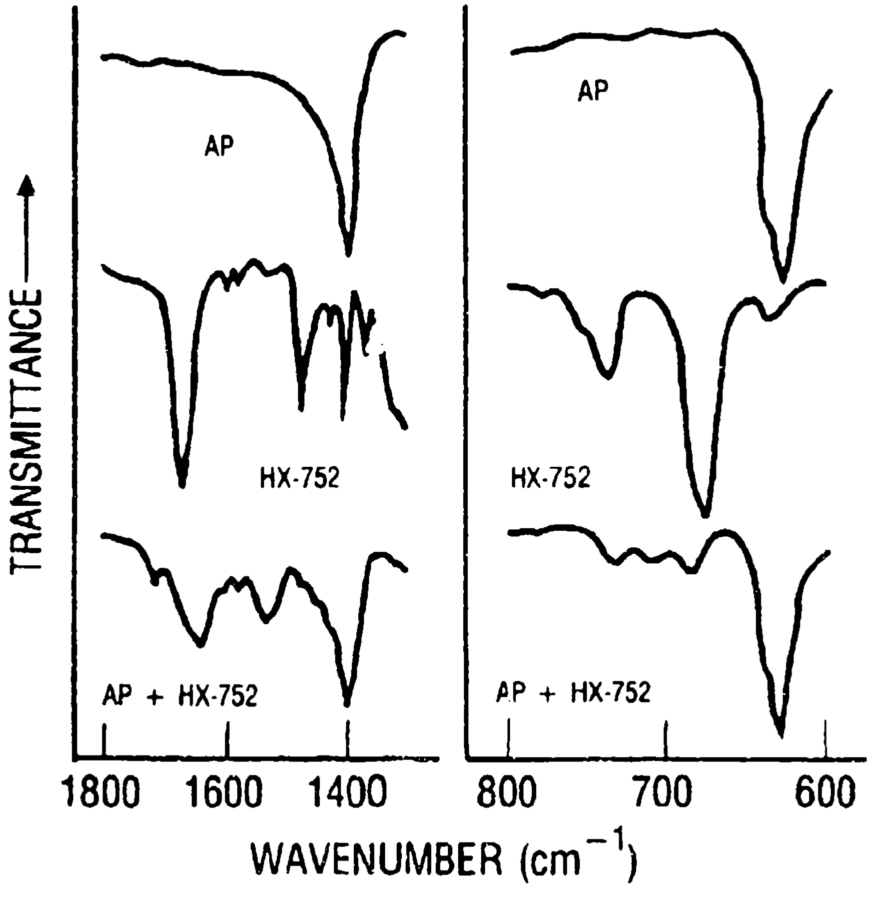


Figure 7. Infrared Spectra of AP, HX-752, and AP + HX-752

V. CONCLUSIONS

The case bond liner system has evolved over time into an increasingly complex set of chemical formulations that can make a specific source of failure nearly indeterminable. The barrier material is designed as a topcoat but is being used as an interlayer between the insulation and the liner. As such, it must not only provide barrier properties to prevent diffusion from adjacent layers but must provide a surface compatible for adhesion to the liner. Thus, it appears to be very important to carefully control curing conditions of the barrier for optimum interfacial adhesion. Since the liner and propellant formulations both contain R-45M, the rate of cure of the barrier can impact the interfacial bonding at both the barrier-liner interface and the liner-propellant interface without necessarily affecting the ultimate mechanical properties of either liner or propellant. This is due to the relative difference in diffusion rates vs the rate of cure of R-45M, resulting in a change in the chemistry at the liner-propellant interface that can lead to weak interfacial bonding. The current state of case bond liner systems suggests that in the absence of invasive moisture, the rate of cure of each of the layers should be known in order to define the degree of cure acceptable for adequate bonding in the interfacial zones. To assure more reliable bonding, it is strongly recommended that the specification limits for the processes employed in these systems be tightened. Studies involving those variables found to be the most sensitive should be addressed initially. With the present multiprocess systems, the more that the parameters involved approach their specification limits during processing, the more likely the potential for failure becomes statistically significant. Even though each process may be within specification, the existence of more than one processing variable that is operating near its specification limit can be overlooked. This is where the overall process is in jeopardy. Fortunately, this system is very forgiving and should give acceptable results much of the time. However, a narrowing of the processing parameters based on the degree of cure should ensure good liner interfacial properties.

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