DREV M-2252/72
PROJ. 46-60-05

DECLASSEMENT NON AUTOMATIQUE
NO AUTOMATIC DOWNGRADING

DI[redacted]

EXEMPLAIRE:
COPY: 37

AN INVESTIGATION OF PROPELLANT/LINER BOND FAILURES IN BLACK BRANT VB ROCKET MOTORS (U)

by

G.L. Duchesne

CENTRE DE RECHERCHES POUR LA DEFENSE

DEFENCE RESEARCH ESTABLISHMENT

VALCARTIER

Québec, Canada

November/novembre 1972

CAUTION

This information is furnished with the express understanding that:

a) It will be used for defence purpose only.
b) It will be afforded essentially the same degree of security protection as provided by the Canadian Department of National Defence.
c) Proprietary and patent rights will be respected.
d) It will not be released to another nation without specific approval of the Canadian Department of National Defence.

AVERTISSEMENT

Les renseignements ci-inclus sont fournis à la condition expresse:

a) qu'ils serviront à des fins de défense seulement,
b) qu'ils feront essentiellement l'objet des mêmes mesures de protection que celles qui sont assurées par le Ministère de la défense nationale du Canada,
c) que les droits de propriété personnelle et industrielle seront respectés,
d) qu'ils ne seront pas communiqués à un autre pays sans l'autorisation explicite du Ministère de la défense nationale du Canada.

DREV M-2252/72
PROJ. 46-60-05

DECLASSEMENT NON AUTOMATIQUE
NO AUTOMATIC DOWNGRADING

[redacted]

AN INVESTIGATION OF PROPELLANT/LINER BOND FAILURES IN BLACK BRANT VB ROCKET MOTORS (U)

by

G.L. Duchesne

CENTRE DE RECHERCHES POUR LA DEFENSE

DEFENCE RESEARCH ESTABLISHMENT

VALCARTIER

Tel: (418) 844-4271

Québec, Canada

November/novembre 1972

RESUME

Depuis quelque temps, Bristol Aerospace Limited (BAL) fait face à un manque d'adhésion entre le propergol au polyuréthane (PU) et l'inhibiteur latéral au PU dans le moteur-fusée Black Brant VB (BBVB). Ce moteur, fabriqué à l'usine de BAL de Rockwood, fut mis au point conjointement par BAL et Aerojet General Corporation. En réponse à une demande de BAL, le CRDV accepta d'étudier la chimie de ce système, de rechercher les causes du décollement et de suggérer certaines rectifications. Cette étude comprend un examen de la documentation fournie par BAL, des consultations avec les chimistes et ingénieurs du CRDV et une visite à Rockwood et Winnipeg pour s'entretenir avec le personnel de BAL. Jusqu'à présent, aucune cause unique du décollement n'a pu être décelée; on est plutôt enclin à expliquer la situation actuelle par un ensemble de facteurs dont, l'humidité présente dans les ingrédients et ajoutée pendant la fabrication, la dissymétrie du bloc de propergol, les contraintes engendrées par le rétrécissement du bloc au cours de la formation des liaisons chimiques, les contraintes thermiques causées par le refroidissement et le cisaillement appliqué pendant l'extraction du mandrin. Certaines améliorations pourraient être obtenues en ajustant les compositions de l'inhibiteur et du propergol et en réduisant l'humidité absorbée par l'inhibiteur. A long terme, on pourrait envisager l'utilisation d'un nouveau tandem propergol/inhibiteur pour le moteur.

ABSTRACT

The Black Brant VB (BBVB) rocket motor, jointly developed by Bristol Aerospace Limited (BAL) and Aerojet General Corporation and manufactured at BAL's Rockwood plant, has recently shown a lack of adhesion between the polyurethane (PU) propellant and the PU liner. As a result of a BAL request, DREV agreed to review the chemistry of the liner/propellant system, to investigate the possible causes of the lack of adhesion and to suggest possible corrective measures. The DREV investigations included an examination of BAL documentation, discussions with DREV chemists and engineers and a visit to Rockwood and Winnipeg for discussions with BAL personnel. To date, no single factor has been pinpointed as the sole cause of debonding between the liner and the propellant. It appears likely that a number of factors have led to the present situation, including the moisture present in the ingredients and added during processing, the asymmetry of the propellant grain, the shrinkage stresses generated in forming the chemical bonds, the thermal stresses due to cooling of the grain and the shear stresses applied during core extraction. Some improvements could be obtained by certain adjustments to the liner and propellant formulations and by reducing the amount of moisture absorbed by the liner. On a longer term basis, the introduction of a new propellant/liner system should be considered for the motor.

TABLE OF CONTENTS

1.0 INTRODUCTION

The Black Brant VB (BBVB) motor was developed jointly by Bristol Aerospace Limited (BAL) and Aerojet General Corporation (AGC). The BBVB motors are manufactured at BAL's Rockwood plant. During recent months, a lack of adhesion has been observed between the liner and the propellant. As a result of a BAL request (Telecon between Mr. A.W. Fia, Vice-President, Rocket and Space Division, BAL and Dr. W.G. Brownlee, Director Propulsion Division, DREV), DREV agreed to carry out the following tasks:

i) review the chemistry of the liner/propellant system;
ii) investigate the possible causes of the lack of adhesion; and
iii) suggest possible corrective measures.

The DREV investigations (carried out by G.L. Duchesne, Leader Process Engineering Group, Rockets Section) consisted of:

i) an examination of BAL documentation (ingredient and product specifications, manufacturing procedures, drawings, etc.);
ii) a review of relevant available literature on polyurethane (PU) propellants and liners;
iii) discussions with DREV chemists and engineers; and
iv) discussions with BAL personnel during a visit to the Rockwood and Winnipeg plants on 27 and 28 September 1972; the discussions were held with Messrs. A.W. Fia, W.E. Robinson, W.A. Bergman, C.F. Fuller, J.S. Lazar, D. Koga, D.E. Mathers and L.S. Graham.

This report briefly describes the BBVB rocket motor and the chemistry of the particular propellant/liner system, summarizes the results of discussions with BAL personnel and suggests possible corrective measures for the debonding problem.

2.0 MOTOR DESCRIPTION AND DEBONDING LOCATION

The BBVB motor has a diameter of 17 in and a length of 180 in. The polyurethane (PU) propellant (designated ANP-2872 J MOD 4) used in the motor was developed by Aerojet General Corporation (AGC). The propellant grain has a cylindrical perforation (5-in diameter) for one third of the motor length at the head-end; a diametrical slot extends over the remaining length of the grain.

The wall insulation consists of phenolic asbestos (42 RPD) facing the two ends of the slot, covered by Gen-Guard V-44 over the entire interior surface of the casing; a brushcoat liner (SR-746) is applied over the V-44. During the installation procedure, the insulated casing is conditioned for 5 hours at 110°F and 20-24% relative humidity (R.H.) prior to liner application. The SR-746 liner (also developed by AGC) is applied over the lightly abraded V-44 surface, at 110°F and 20-24% R.H.

The debonding was observed immediately after propellant curing in the areas facing the two ends of the slot. In the X-ray photographs, gaps as wide as 1/8-in were visible between the liner and the propellant grain.

3.0 CHEMISTRY OF PROPELLANT/LINER SYSTEM

The ANP-2872 propellant is a polyurethane-based formulation containing eight solid ingredients and eight liquids. The solids are: two classes of ammonium perchlorate oxidizer (AP), two classes of aluminum, phenyl-beta naphtylamine (PBNA), carbon black, sulfur and ferric acetyl acetonate (FeAA) curing catalyst. The eight liquids are:

poly (1,2-oxypropylene) glycol, (PPG);
poly (1,4-oxybutylene), a diol designated LD-124;
hexane triol/propylene oxide adduct (LHT-240), a triol with a molecular weight of 700;
triethanolamine, a bonding agent;
polyoxyethybene monolaurate, a wetting agent;
diethyl hexylazelate, a plasticizer;
2,4-tolylene diisocyanate (TDI); and
silicone fluid DC-200.

The first five listed liquids have chemically active OH groups which form polyurethane links with the NCO groups of TDI. In addition, the bonding agent triethanolamine chemically reacts with AP yielding a dense layer of OH groups near the AP surface. These OH groups later form chemical links with the binder matrix by reacting with NCO groups.

The SR-746 liner is made of 50 percent by weight of a premix and 50 percent of a prepolymer. The premix contains zinc oxide filler and three liquids having OH groups (PPG, poly (1,4-oxybutylene) and castor oil); the prepolymer contains PPG, TDI and FeAA.

According to AGC-36026/31 specification, the ANP-2872 propellant composition is fixed (frozen) on a weight basis and the only compositional variations should come from the acceptance tolerances on the raw materials or intermediate products (premix, prepolymer, etc) mainly in relation to OH groups concentration and water content.

According to Arendale [1], chemists and process engineers involved with polyurethane propellants should pay close attention to the control of moisture in the ingredients and during processing. Water reacts with the isocyanate according to:

$$R\text{-}NCO + H_2O \rightarrow CO_2 \uparrow + R\text{-}NH_2$$

The carbon dioxide generated during the curing cycle creates spongy propellant and liner.

In examining the chemistry of the ANP-2872 propellant and SR-746 liner, it was of interest to determine the NCO/OH ratio in both

../3

materials by assuming i) fully dry ingredients and ii) the maximum amount of moisture permitted in the specifications. The results are summarized below.

NCO/OH Ratios in Propellant and Liner

	Typical	Range
Propellant - dry ingredients	1.028	1.008 - 1.051
Propellant - wet ingredients	0.832	0.816 - 0.851
Liner - dry ingredients	1.071	1.057 - 1.084
Liner - wet ingredients	0.955	0.943 - 0.969

Four permutations are possible depending upon the moisture content of the ingredients:

a) NCO-rich propellant with NCO-rich liner
b) NCO-rich propellant with OH-rich liner
c) OH-rich propellant with NCO-rich liner
d) OH-rich propellant with OH-rich liner

Although chemical links between the propellant and the liner are probably formed during the entire curing cycle of the propellant for each of the above four cases, conditions (b) and (c) offer better chances of success. DREV chemists prefer case (b) on the basis that an OH-rich liner would be less sensitive to moisture than an NCO-rich formulation. Of course, in selecting the NCO/OH ratios for a propellant/liner system, consideration must be given to the mechanical properties and processing characteristics of both components. However, such products also offer other means for tailoring the mechanical properties by changing the diol/triol ratio in the propellant or adjusting the concentration of the reinforcing filler in the liner.

4.0 CONSIDERATIONS ARISING FROM BAL DISCUSSIONS

During the course of the discussions at Rockwood Plant and Winnipeg, the operating procedures and quality control records were thoroughly reviewed with the immediate objective of finding changes or trends in properties which could explain the debonding at the propellant-liner interface. The following points arose:

(1) Most of the BBVB motors showing bond failures were processed during the summer months, corresponding to the most humid period of the year.

(2) The debonding was observed immediately after curing of the propellant; however, it could not be established whether this debonding took place before or after core removal, before or after cooling of the grain, etc.

../4

[redacted]

(3) Mechanical properties of approximately 90 batches of ANP-2872 propellant were excellent, with strength at maximum load (σ_m), elongation at maximum load (ε_m) and initial modulus (E) averaging 140-200 psi, 60-75 percent and 400-700 psi respectively. Although batch-to-batch variations were apparent, no trend could be detected between the mechanical properties of the propellant samples tested at Rockwood and the batches showing bond failures. It was noted, however, that five or six years ago ANP-2872 propellant had a σ_m of 140 psi whereas the average σ_m was close to 200 psi for the more recent batches. The initial modulus obviously followed the same trend.

(4) Mechanical properties of the SR-746 liner over the operating temperature range of the BBVB rocket motor are not known and BAL is not equipped for rapidly determining them. As indicated by double plate bond tests, the tensile strength of the liner is probably lower than that of the ANP-2872 propellant. According to many rocket motor designers, this is not a desirable feature.

(5) Double plate tests carried out as quality control on all the propellant batches generally showed good propellant/liner adhesion with tensile strengths of better than 120 psi (Appendix 'A'). Most of the bond failures were clean peel at the SR-746/propellant interface and/or cohesive in the propellant, with either a thin film of propellant left on the liner (type P_1) or a thicker propellant layer (type P_2). The effect of conditioning the V-44 insulant under relatively high humidity (20-24% R.H. at 110°F) is also discussed in Appendix 'A'. Recent adhesion tests at Rockwood to evaluate the conditioning of V-44 and curing of SR-746 liner under three different humidity conditions (six permutations) did not show any significant reduction in the tensile strength of the propellant/liner bond, although the mode of failure may have changed from one specimen to the other.

(6) The possibility was not discarded that volatiles are trapped underneath the insulating materials (42 RPD and V-44). These volatiles are present in the P-4 metal primer, 1209 cement, Durez/MEK solution and V-44/MEK solution, all used for metal casing preparation or gluing of the insulants.

(7) To conform to recent recommendations from Aerojet General Corp., BAL has increased the liner thickness from 0.015 to 0.030-0.035 in and has conditioned V-44 insulant, for 5 hours at 20-24 percent R.H. and 110°F prior to liner application.

(8) The degree of dispersion of the prepolymer in the premix, a component of SR-746 liner, was questionned since the mixing time of 2-3 minutes specified in process specification sheet AGC-36098 and O.P. No. 207 seems unusually short. It was noted that the potlife of 15 minutes for SR-746 is also very short, which obviously does not leave much time for brush application of the liner.

../5

(9) The forces required to pull the cylindrical part of the core and the two slots were not known; the core is normally coated with polyethylene wax for release purposes. The core is pulled at 100°F, i.e. 10°F below the cure temperature of the propellant.

5.0 ADDITIONAL CONSIDERATIONS

(1) Water reaction with isocyanate groups is highly undesirable in a polyurethane propellant/liner system on account of the CO_2 formation and adverse effects on the mechanical properties of the two products. According to Oberth and Bruenner [2]:

"This degradation of properties is caused by the accumulation of moisture on the surface of the oxidizer crystal, thus creating a low modulus layer which envelops the particle. In essence, this means that the bond between oxidizer and binder is destroyed, and dewetting will commence at low stress levels with commensurate loss of mechanical properties. Small quantities of absorbed moisture (0.1% or less) cause this effect."

The NCO-rich liner rapidly adsorbs water at the surface. In addition, the water already adsorbed in the V-44 probably migrates through the liner. This moisture in turn prohibits a thin layer of propellant or liner from curing properly. This may provide a weak boundary layer which leads to a failure much below the strength of either the propellant or liner.

(2) The above comment is somewhat contradicted by the results of the double plate tests (Section 4, No. 5). It should be noted; however, that the geometry of a double plate specimen is different from that of the propellant grain. In addition, the shrinkage stresses resulting from chemical links are volume dependant. Thus, the shrinkage stresses accumulating during curing may considerably interfere with a strong bond formation at the propellant/liner interface. This is particularly applicable to ANP-2872 propellant, which contains shorter molecular weight ingredients at the beginning of vulcanization, than modern polybutadiene propellant components. It has been estimated that ANP-2872 formulation requires three times more chemical links than a typical polybutadiene propellant and therefore generates more severe shrinkage stresses during cure.

(3) The debonding of an already weak bond is more likely to occur in the areas of the motor having the highest stress concentrations; this is close to the ends of the slot.

(4) The shear stresses exerted on the interface during core extraction are a possible contributory factor.

(5) The stresses resulting from grain cooling to ambient or lower temperature must also be considered. A grain stress analysis could predict the distribution of such stresses inside the motor provided that appropriate WLF (Williams, Landel, Ferry) curves were available.

../6

[redacted]

6.0 CONCLUDING REMARKS

To date, no single factor has been pinpointed as the sole cause of the debonding between the SR-746 liner and the ANP-2872 propellant in BBVB rocket motors. It appears likely that a number of factors contribute to the situation, including the moisture present in the ingredients or added during processing, the asymmetry of the propellant grain, the shrinkage stresses generated in forming the chemical bonds, the thermal stresses due to cooling of the grain and the shear stresses applied during core extraction.

The following course of action is suggested in order to resolve the debonding problem:

1. Determine the mechanical properties of the liner over the operating temperature range of the rocket. DREV could carry out this investigation using samples prepared by BAL.

2. Depending on the results of (1), adjust the liner formulation for a longer pot life, better mechanical properties and also to obtain an OH-rich mixture.

3. Protect the insulated casings against moisture and apply the liner in a low relative humidity environment.

4. Adjust the ANP-2872 propellant formulation to obtain an NCO/OH ratio of 1.05 to 1.07, assuming dry ingredients; adjust the tensile strength to 120-140 psi (room temperature) by reducing the amount of triol.

5. Determine when and where debonding takes place by examinations at the following stages:

   i) one or two days before the end of cure at 110°F,
   ii) at the end of cure at 100°F,
   iii) after pulling the cylindrical part of the core (noting the force required),
   iv) after pulling the two slots of the core (noting the force required), and
   v) after cooling the grain to room temperature.

6. Defer consideration of a grain stress analysis, at least until the foregoing results are at hand; the absolute accuracy of such analyses is not high and the principal benefits result when relative stress/strain distributions are of interest, as for example when considering a new grain design.

7. On a longer term basis, consider an improved propellant/liner system, which would necessarily involve a requalification program for the motor.

7.0 REFERENCES

[1] Arendale, William,L., "Chemistry of Propellants Based on Chemically Crosslinked Binders," Advances in Chemistry Series 88, Amer. Chem. Soc., 1969.

[2] Oberth, A.E. and Bruenner, R.S., "Polyurethane-Based Propellants," Advances in Chemistry Series 88, Amer. Chem. Soc., 1969.

../8

APPENDIX A

bristol aerospace limited

CLASSIFICATION:	DATE September 14, 1972
TO Mr. W.A. Bergman	REF.
FROM D.E. Mathers	COPIES W.E. Robinson J.S. Lazar Q.C. File
SUBJECT DOUBLE PLATE TESTS OF THE BOND BETWEEN ANP 2872 J MOD 4 (propellant/ SD746 (Washcoat)/V-44 (rubber liner)	

.727

The collected data from samples tested at Rockwood has been analysed to demonstrate the bond strength and the mode of failure for different methods of Washcoat curing.

The tests were carried out to Q.C. Method M-0083 and the interpretation methods incorporated in this specification. Three samples were tested per batch of propellant; the mean strength being taken for the predominant failure mode for the samples.

Values have been incorporated for samples, which failed due to glue failure. It must be noted that the mean bond strength and the standard deviation are slightly lower than the true values as the bond strength on these samples was not reached when the glue failed.

Cure Condition for SD746 Washcoat	No. of Propellent Batches Tested	Bond Strength psi		Glue Failure No. of Batches	TYPE OF FAILURE Bond Failure (%)			
		Mean	Standard Deviation		Clean Peel V-44/SD746	Clean Peel SD746/Propt.	P1	P2
1) No Humidity Control-Chamber Nitrogen purged	47	119.5+	29.4+	4	4.7	46.5	37.2	11.6
2) 16-20% RH at 110°F.	33	149.5+	30.9+	8	8.0	44.0	36.0	12.0
3) 20-24% RH at 110°F.	6	119.5+	25.0+	1	60.0		40.0	

NOTE: P1 failure is failure in the propellant leaving less than 1 mm of propellant on the washcoat surface.

P2 failure leaves more than 1 mm of propellant on the washcoat surface.

bristol aerospace limited

CLASSIFICATION:	DATE
TO	REF.
FROM	COPIES
SUBJECT	

1727

The processes used for chamber preparation and application of SD746 had the following humidity conditions.

	Batches	Chamber Preparation Conditions	SD746 Application Conditions
1)	Up to batch 465 (excluding 463)	Nitrogen purge whilst heating to 110°F.	Nitrogen purge whilst curing at 110°F.
2)	Batch 467 to 513 (including 463)	Nitrogen purge whilst heating to 110°F.	16 - 20% RH whilst curing to 110°F.
3)	Batch 514 onwards	20 - 24%RH whilst heating to 110°F.	20 - 24% RH whilst curing to 110°F.

CONCLUSIONS

1) Changing the cure condition from 1 to 2 increased the bond strength without changing the failure mode appreciably. The undesirable clean peel failure is still evident, however, in up to half of the batches.

2) As the number of batches processed as in 3 above is small, the values for bond strength are not accurate. The drastic change in the mode of failure should be noted as there is a clear indication of an unusual mode of failure namely between the V-44 and Washcoat. This is probably due to the conditioning before washcoat application with 20 - 24% RH air (at 110°F). It maybe desirable to condition the V-44 in contact with dry nitrogen to rectify this.

D. E. Mathers

D.E. Mathers,
Q.C. Engineer.

DEM:aaf

INTERNAL DISTRIBUTION

1 - Director-General
1 - Deputy Director-General
10 - Document Library
1 - Military Assistant
1 - Director Plans and Programs Centre
1 - Director Armaments Division
1 - Director Data Systems Division
1 - Director Electronics Division
1 - Director Experimental Division
1 - Director Propulsion Division
1 - Mr. G.L. Duchesne (Author)
1 - Mr. J.Y. Bélanger
1 - Dr. G.H. Kimbell
1 - Mr. F. Jackson
1 - Dr. R. MacDonald
1 - Dr. M. Tremblay
1 - Dr. G. Perrault
1 - Dr. R. Lavertu
1 - Dr. K.S. Kalman
1 - Mr. J.F. Drolet
1 - Dr. F.A. Christie
1 - Mr. D. Smith
1 - Mr. G. Couture
1 - Mr. J. Ratte
1 - Mr. C. Shea

EXTERNAL DISTRIBUTION

1 - DSIS
1 - DRB Report Collection
1 - VC/DRB
1 - DC(O)
1 - DC(Sc)
1 - CSP
1 - C Plans
1 - SA/VCDS
1 - CRRD
1 - CDRS(L)
1 - CDRS(W)

6 - Bristol Aerospace (1968) Limited
(3 - Mr. A.W. Fia &
3 - Mr. W.E. Robinson)

UNCLASSIFIED

[redacted]

8801 a	✓	2	Copy #	1
b	✓	EAW	Information Scientist	
8802 a	✓	DSIS/DIST		
b				
c				
8803	✓	DEC 18 1972	90	H
DSIS ACCN #		73-00538		

DEFENCE RESEARCH BOARD
DEFENCE SCIENTIFIC
INFORMATION SERVICE
NATIONAL DEFENCE HEADQUARTERS
OTTAWA, ONTARIO
K1A 0Z3

ABSTRACTED BY
EAW
DEC 28 1972

2364

UNCLASSIFIED