THE EVALUATION AND VALIDATION OF NEW CREEP BARRIER FILMS FOR PREVENTION OF OIL LOSS BY MIGRATION

Matthew R. Hampson, Ben Wardzinski

ESTL, ESR Technology (a Hyder Consulting Group company), 202 Cavendish Place, Birchwood Park, Warrington, WA3 6WU, UK, Email: matthew.hampson@esrtechnology.com

ABSTRACT

Creep barrier films are used to prevent loss of oil by surface migration. This paper gives an overview of studies to select, characterise and validate creep barrier materials for spacecraft mechanisms [1].

One of the more commonly used materials, Fluorad FC-725, is no longer manufactured, and there is a need to identify a replacement.

A survey of available materials was carried out, and after a series of trial tests, three materials were down-selected for the validation exercise: two new materials - 3M Novec 2708 and Dr Tillwich E2 Concentrate – alongside the obsolete Fluorad FC-725 used as a baseline.

A validation procedure is defined, which may be applied to other new creep barrier materials in future. Testing confirmed that either of the new materials would be suitable for use.

1. BACKGROUND

The surface migration of oils is one of the major mechanisms by which oil is lost from a contact area in tribological components, potentially limiting mechanism life as well as risking contamination of nearby sensitive components. Oil migration may be minimised by the use of surface coatings known as "creep barriers" to restrict the movement of oils to adjacent surfaces [2].

The particular feature of creep barriers which allows them to function in the way that they do (i.e. prevent the spread of oil) is their low surface energy. When a drop of oil is placed onto creep barrier, it forms a bead-like drop due to the low interfacial energy. In contrast, when a drop of oil is placed onto a metal surface, the oil initially forms a very flat drop with a low contact angle due to the relatively high interfacial energy.

The type of creep barrier used in space applications is based upon a fluorinated methacrylate polymer, supplied in a solution which can be painted onto a surface. The polymer coatings generally have surface energies in the range 11-12 mN/m which is lower than the surface tension of all existing space oils. According to manufacturer-supplied data, such oils typically have surface tensions in the range 17-33 mN/m and are thus theoretically incapable of wetting the barrier material.

One of the most commonly used creep barrier products, Fluorad FC-725 is no longer commercially available, and there was therefore a need to identify both suitable candidate replacement materials and a test methodology for their performance validation.

2. SELECTION OF MATERIALS

A number of products suitable for use as creep barriers are currently available, produced by a range of manufacturers.

3M produce several products which may be used as creep barriers, under the Novec brand name. These are primarily marketed as coatings for the protection of electronic components, but their properties also make them ideally suited for use to prevent oil creep. The Novec EGC 1700 product is quite well established in the space industry and has some heritage at ESTL [3], but a newer product from 3M is the Novec 2700 series, with a variety of polymer concentrations available.

Nye Lubricants have a range of products named Nyebar which were also considered, but were not included in this validation exercise due to concerns over ITAR (International Traffic in Arms Regulations) regulatory status. However, Nyebar LV 2% has previously been tested at ESTL [4].

Dr Tillwich, a European manufacturer, produces a range of creep barrier products. ESTL initially tested E2/50 FE60, but it became apparent that a product with higher solid content than their existing products would be desirable. ESTL made this request to Dr Tillwich which resulted in the introduction of a new product Antispread 'E2 Concentrate', which has since been made available commercially.

A product under development by CNES was also considered in the initial stages of our activity, although the development was subsequently abandoned.

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Since most of the available products are based on the same type of polymer, technical performance is expected to be broadly similar, although it must be verified by testing. Other considerations such as availability are also important factors in selecting a creep barrier material. It is recognised that a European sourced material would be preferable to many users in the industry.

A down-selection process was performed, considering the suitability of each of the candidates and results of informal trial tests. This resulted in the selection of two materials for the full validation program: 3M Novec 2708 and Dr Tillwich E2 Concentrate.

3. TEST PROGRAM OVERVIEW

A comprehensive test program was designed to provide a validation process for creep barriers with regard to their suitability in space applications, enabling an informed choice to be made depending upon the intended application. The candidate materials were subjected to a series of test stages to characterise their behaviour as applicable to use in space, including measurement of:

- Outgassing properties.
- Chemical stability during storage.
- Stability following prolonged exposure to air and vacuum.
- Stability during thermal cycling under vacuum.
- Effectiveness in arresting oil creep under gravity (in vacuum).

As well as the two materials selected above, the discontinued heritage material, Fluorad FC-725 was also included to provide a benchmark comparison.

Selected tests were also performed on other materials, as part of initial evaluation work and results are included here where relevant.

4. CHARACTERISATION TESTS

Creep barrier materials were tested by several methods to characterise their behaviour as applicable to use in space. This included: contact angle measurements, adhesion tests, IR spectroscopy, outgassing property tests and visibility checks.

4.1. Compatibility with space oils

An initial screening test was carried out to confirm that the creep barriers were chemically compatible with two of the most commonly used space oils, Fomblin Z25 (a perfluorinated polyether) and Nye 2001a (a multiply alkylated cyclopentane). A drop of oil was placed onto creep barrier film and heated to 100 °C for 24 hours in laboratory air. The sample was then visually inspected to confirm the oil remained as a bead on the surface, and to check for signs of degradation to the coating which would indicate undesirable chemical reactions.

This test showed no problems with any of the fluorinated methacrylate polymer films. This quick, simple test could be used to assess new combinations of chemical types – either on the introduction of a chemically different creep barrier or a new type of oil.

4.2. Contact angle measurements

A quantitative measure of creep barrier efficacy was obtained by measuring contact angle, using a drop shape analysis instrument (Fig. 1).

Figure 1. Krüss DSA25S drop shape analyser purchased by ESTL for contact angle measurements.

An effective creep barrier will not be wetted by an oil, instead the oil should remain as a bead on the surface. The contact angle between the drop and the substrate at the edge of the drop can be used a measure of the interfacial tension.

The contact angle of two space lubricant oils (Fomblin Z25 and Nye 2001a) applied onto creep barrier films was tested. Creep barriers were applied onto 440C steel plates (R_a <0.3 μm), drops of oil deposited and the contact angle measured, the results are shown in Tab. 1.

A higher contact angle of oil droplets indicates a more effective creep barrier, since the oil wets the surface less effectively. It is seen that the general trend is for creep barriers with higher solid contents to give larger contact angles. This is easily understood, since the creep barriers are generally similar in chemical nature, and therefore the solid content is the main difference between them. Fluorad FC-725 has the highest solid content of the tested materials and gave the highest contact angles.

Table 1. Oil contact angles.

Creep Barrier Product	Solid Content (%)	Z25 Contact Angle (degrees)	Nye 2001a Contact Angle (degrees)
3M Novec EGC 1700	2	37.7	73.2
3M Novec 2704	4	37.2	73.5
3M Novec 2708	8	37.7	73.9
Dr Tillwich E2/50 FE60	<0.2	34.1	64.1
Dr Tillwich E2 Concentrate	2	34.4	75.0
Fluorad FC-725	15	42.9	76.1

4.3. Infrared Spectroscopy

Infrared (IR) spectroscopy was used to chemically analyse the creep barrier films (Fig. 2). The spectra for the three materials confirm that the chemical composition is similar.

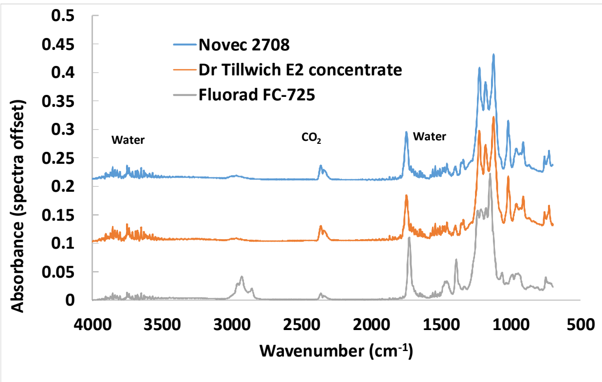


Figure 2. Infrared spectra of creep barriers.

Spectra were also recorded during the stability tests (Section 5) and showed no evidence of degradation of the films after 12 months storage.

4.4. Applying creep barrier and adhesion to substrate

The function of creep barriers is dependent on achieving the correct thickness of material in the desired location. The materials which we tested are supplied as polymers in a solvent, and there are two main application techniques for applying the films – immersion and brushing. The immersion method is suitable when a whole component is to be treated with a creep barrier. For spacecraft mechanisms it is probably more common for a line of creep barrier film to be required on a component (for example adjacent to a bearing race), in which case a brush is used.

In our tests, films were applied using a consistent method, with a single brush stroke. The thickness of the polymer layer is dependent on the polymer content of the solution – for example 0.5-1µm thickness is typical for creep barriers with 2% polymer content.

The adhesion of the deposited polymer to substrates was tested using a cross hatch adhesion test. This showed no delamination with any of the three tested creep barriers.

4.5. Functional tests

A direct measurement of the ability of creep barriers to prevent oil migration was devised. Creep barriers were painted onto sample plates to block the flow of an oil drop under gravity (Fig. 3).

Figure 3. Oil drop enclosed by creep barrier boundary on a test plate.

Six creep barrier materials were tested in a short duration (24 hour) test, to allow rapid evaluation of their performance. Stainless steel plates were used with Fomblin Z25 oil, and the plates were held at 100 °C in air for 24 hours.

Table 2. Functional test results – 24 hours, 100 °C in air.

Creep barrier product	Oil migration prevented		
	Initially	After 1 hour	After 24 hours
3M Novec EGC 1700	Yes	Yes	Yes
3M Novec 2704	Yes	Yes	Yes
3M Novec 2708	Yes	Yes	Yes
Dr Tillwich E2/50 FE60	Yes	Yes	No
Dr Tillwich E2 Concentrate	Yes	Yes	Yes
Fluorad FC-725	Yes	Yes	Yes

All of the tested materials passed this test (results in Tab. 2), with the exception of Dr Tillwich E2/50 FE60. It was thought that the failure of E2/50 FE60 was related to the material's exceptionally low solid content (<0.2%). This theory seems to be confirmed by the fact that the chemically identical Dr Tillwich E2 Concentrate (with 2% solids) performed satisfactorily.

Longer term functionality was tested on three substrate materials - aluminium, titanium and stainless steel. The plates were held at a 5° angle for 3 months, under high vacuum at 100°C. The three creep barriers tested were successful in preventing oil migration with all the combinations of substrates and oils listed in Table 3.

Table 3. Functional test results – 3 months, 100°C, vacuum.

Creep barrier product	**Substrate material**	**Substrate surface roughness, Ra (µm)**	**Oil migration prevented**	
			Fomblin Z25	**Nye 2001a**
Fluorad FC-725	Steel – AISI 440C, passivated	0.3	✓	✓
		3	✓	✓
	Titanium alloy, Ti6Al4V AMS4928	0.3	✓	✓
		3	✓	✓
	Aluminium alloy, AL7075 T7351, Alochrom 1200	0.3	✓	✓
		3	✓	✓
3M Novec 2708	Steel – AISI 440C, passivated	0.3	✓	✓
		3	✓	✓
	Titanium alloy, Ti6Al4V AMS4928	0.3	✓	✓
		3	✓	✓
	Aluminium alloy, AL7075 T7351, Alochrom 1200	0.3	✓	✓
		3	✓	✓
Dr Tillwich E2 Concen-trate	Steel – AISI 440C, passivated	0.3	✓	✓
		3	✓	✓
	Titanium alloy, Ti6Al4V AMS4928	0.3	✓	✓
		3	✓	✓
	Aluminium alloy, AL7075 T7351, Alochrom 1200	0.3	✓	✓
		3	✓	✓

4.6. Outgassing

The outgassing of three creep barrier polymers was tested in accordance with the relevant ECSS procedure [5]. The samples tested were polymer solids after evaporation of the carrier solvent, representative of applied creep barrier films.

Results (Tab. 4) are reported in terms of TML (Total mass loss, including water vapour out-gassing.), RML (Recovered mass loss, mass loss without water vapour) and CVCM (Collected volatile condensable material, i.e. mass re-condensed on a cold collector plate).

Table 4. Outgassing test results.

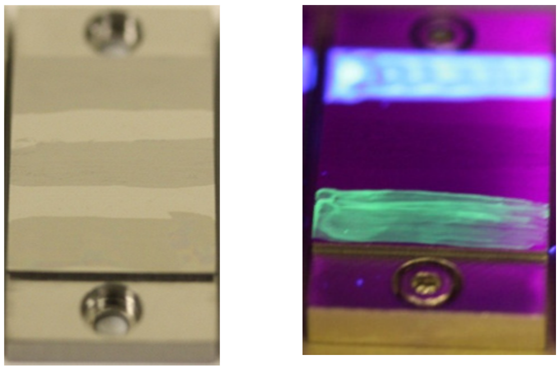
Material	**TML %**	**RML %**	**CVCM %**
Dr Tillwich E2 concentrate	5.55	5.47	0.02
3M Novec 2708	2.24	2.19	0.08
FC-725	5.16	4.94	0.01
ECSS Acceptance limits (General use)	*1.0*	*1.0*	*0.1*

All three of the tested materials met the ECSS acceptance criteria for CVCM, but failed in terms of TML and RML. It may be argued that the high TML and RML values may be acceptable for most applications, due to the small amount of creep barriers applied. It is anticipated that the outgassing observed would only be a problem for extremely contamination critical cases.

4.7. Visibility

The visibility of three creep barriers (FC-725, Dr Tillwich E2 concentrate and Novec 2708) was checked under both ambient and UV lighting (Figure 4).

Fluorad FC-725 contains a UV-fluorescent dye additive, to enable it to be clearly seen under UV light. Novec 2708 contains UV-fluorescent component which is chemically bonded to the fluoropolymer, so that it cannot separately evaporate away. Dr Tillwich E2 does not contain any UV-fluorescent components. As Fig. 4 clearly shows, the UV-fluorescent components aid visibility of the materials, making it easy to confirm that a creep barrier is present.



(a) Ambient lighting (b) UV lighting

Figure 4. Creep barriers on 440C steel. Upper stripe = FC-725, Middle stripe = Dr Tillwich E2, Lower stripe = Novec 2708.

After thermal cycling under vacuum, the fluorescent marker of the FC-725 material was no longer visible. This is attributed to the dye evaporating. In contrast, the fluorescence of the Novec 2708 material was still clearly visible even after thermal cycling.

5. STABILITY

The stability of the creep barriers was assessed by a series of tests.

5.1. Chemical stability of creep barrier solutions

Stability tests were carried out to assess whether the creep barrier solutions degrade in their containers during storage. Oil contact angle measurements, performed in a similar manner to that described previously (Section 4.2) were made on creep barriers deposited from solutions which had been stored in bottles for up to 12 months in laboratory ambient conditions. These tests were performed with:

(a) bottles received from supplier and left unopened.
(b) bottles opened to remove samples.

Both tests showed no deterioration of the creep barrier solutions.

5.2. Chemical stability of creep barrier films

The effect of prolonged exposure to ambient conditions/lab air and thermal vacuum conditions on creep barrier films when applied to a range of metal substrates (aluminium, titanium and stainless steel) was examined. Samples were maintained:

- for 12 months in laboratory air under ambient conditions
- for 12 months under vacuum

The creep barrier films were tested at 3 month intervals by the following methods:

- oil contact angle measurement.
- visual examination for delamination

In addition, IR spectroscopy was carried out on creep barrier films applied to steel plates. This analytical technique was used to check for signs of chemical degradation after storage of 12 months in vacuum, air and nitrogen-purged desiccator condition.

None of the tests showed evidence of deterioration of the creep barrier films.

5.3. Stability of creep barrier films under thermal cycling

The materials were also tested for their stability under thermal cycling. Samples of creep barrier films applied to test plates were subjected to cycles of temperature between -100°C and +100°C in accordance with the relevant ECSS standard [3].

The three creep barriers were tested, in combination with three substrate materials (aluminium, titanium and stainless steel). The following test methods were used to evaluate degradation of samples before and after thermal cycling:

- UV marker visual check (where relevant)
- oil contact angle measurement
- adhesion – checked visually and tested by cross hatch test method.

Testing showed no signs of degradation for any of the materials, with the exception of the reduced visibility of fluorescent marker in FC-725 as previously noted.

6. DEFINITION OF VALIDATION METHOD

A further aim of our work was to develop a methodology to be used for validation of creep barrier materials in future. This could be used to characterise new materials and provide confirmation that they meet acceptable standards for use in spacecraft. The adoption of this standard method, approved by ESA, enables easy comparison between materials. We have defined a procedure which comprises the test techniques described in this paper. Further details including test success criteria are reported in an ESTL report [1].

As an assessment of a new material, we recommend a characterisation process consisting of the following stages:

1. Outgassing property measurements
2. Tests of oil creep under gravity
3. Thermal cycling of creep barrier films.

The above procedure can be carried out in a duration of approximately 4 months. It is suggested that a new product might be considered for implementation in a mechanism development project on completion of this assessment program, if agreed by all parties.

However, formal and complete validation also requires assessment of the longer term stability. The full validation procedure includes the above stages, and the following additional test stages:

4. Chemical stability of creep barrier solution
5. Chemical stability of creep barrier coating

The full validation procedure has a duration of approximately 12 months.

7. DISCUSSION OF RESULTS

Creep barrier products are generally similar in their composition. All of the substances tested here, in common with earlier generation products with known space heritage, contain fluorinated methacrylate polymer dissolved in a volatile solvent.

The performance of a barrier film is dependent on the thickness of polymer film, which in turn is related to the concentration of solids in the solution. This was shown by the contact angle measurements, and the fact that the only creep barrier failure observed was for the very low concentration material, Dr Tillwich E2/50 FE60. Given that the creep barrier film is essentially a solid particulate suspension, a brush-applied film would be expected to have some degree of porosity and non-uniformity. We could speculate that the higher solids concentration not only provides the potential for a more complete coverage of the substrate but may even provide to some extent a physical barrier to migration resulting in a more oleophobic (oil repelling) barrier. Solutions with high solid content are therefore most likely to provide effective creep barriers.

It may also be possible to achieve thicker polymer layers by modifying the application technique. However, this may have consequences for the adhesion of the polymer to the substrate, and so application methods should be verified by testing. In the validation work presented here, all creep barrier films were applied by the same single layer brushing technique.

Our measurements show that in general the oil contact angle on a creep barrier film is not dependent on the substrate material. This leads us to conclude that, provided a sufficiently thick polymer layer is deposited, it is reasonable to expect creep barrier performance to translate well to other similar materials not tested here, for example other stainless steels, titanium or aluminium alloys.

8. CONCLUSIONS

ESTL has conducted an investigation into creep barriers, motivated by the need to identify replacements for the obsolete Fluorad FC-725.

Two candidate materials have been identified, 3M Novec 2708 and Dr Tillwich E2 Concentrate, both of which are chemically similar to Fluorad FC-725 and other heritage creep barrier materials.

A test program for validation of the materials was devised, and testing confirmed that either of the two candidate creep barriers tested here would make a suitable replacement for Fluorad FC-725 for use in space applications.

3M Novec 2708 and Dr Tillwich E2 Concentrate are now considered to be validated by our testing.

It is noted that for European users, an advantage of the Dr Tillwich product is its European origin. However, the technical performance of the 3M product was similar, and also met the requirements. If the user desires a creep barrier with a UV-fluorescent marker to aid visibility then they should choose 3M Novec 2708. The fluorescent marker in Novec 2708 is more resilient to thermal vacuum conditions than that in the heritage, and now obsolete Fluorad FC-725 product.

8.1. Recommendations

ESTL recommends that the ESA approved validation method outlined in this paper (and detailed in our report [1]) is used to validate any other materials under consideration for use as creep barriers.

9. REFERENCES

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