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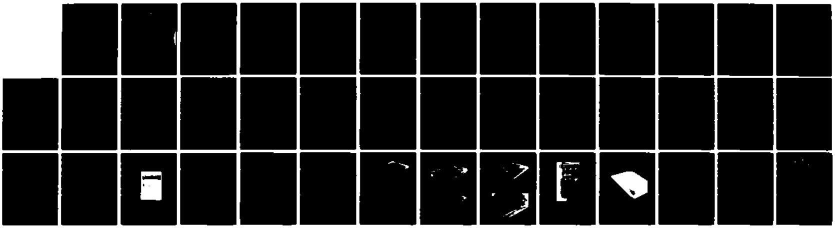

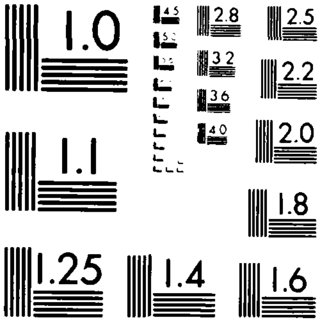

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REPORT

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INTERACTIONS BETWEEN F-111 FUSELAGE FUEL TANK SEALANTS
PART 2. VARIATION IN PERFORMANCE PROPERTIES OF POLYSULFIDES AFTER CONTACT WITH POLYESTER DEGRADATION PRODUCTS

Peter J. Hanhela and D. Brenton Paul

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Interactions Between F-111 Fuselage Fuel Tank Sealants Part 2. Variation in Performance Properties of Polysulfides After Contact With Polyester Degradation Products

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PART 2. VARIATION IN PERFORMANCE PROPERTIES OF POLYSULFIDES AFTER CONTACT WITH POLYESTER DEGRADATION PRODUCTS

1. INTRODUCTION

Fuel storage in the F-111 aircraft is maximised through use of integral tanks formed by sealing available cavities in the fuselage, wings and vertical stabiliser. For the fuselage fuel tanks a multiple barrier design was introduced (Figure 1) which involved two types of sealant. Fasteners and seams within the tanks were coated with fillets of polysulfide, the conventional sealant for applications which involve direct contact with fuel. Faying surfaces and voids, however, which were expected to experience greater aerodynamic heating, were sealed with a thermally resistant polyester material of undisclosed formulation which was designated as EC 5106. This sealing concept was intended to provide the capability to counter fuel leaks by introduction of sealant from the exterior of the aircraft through a series of injection holes. These allow sealant to enter grooves milled into faying surfaces and pass into the cavity responsible for the leak.

Deficiencies associated with the polyester sealant have prevented satisfactory evaluation of this sealing system. In service the EC 5106 sealant underwent hydrolytic degradation which caused the material to change from a firm elastomer to a viscous resin. Contact between the fillet seals and these polyester degradation products ultimately leads to rupture of the polysulfide. A contributing factor in this process has been thought to be expansion pressure which is generated when the polyester degrades within the confines of the joint surfaces. Following recognition of this process, EC 5106 was superseded by a modified polyester, EC 5146, with improved hydrolytic stability. Even with this replacement sealant degradation occurred at an unacceptable rate [1].

The polyester materials cannot be removed from the aircraft structure by practical means. A repair procedure has been developed [2,3] which involves the physical separation of the polyester and polysulfide materials by a flexible epoxy coating. This requires prior removal of polysulfide, application of the epoxy coating, and a reseal with a two part polysulfide conforming to MIL-S-83430. The long term effectiveness of this process cannot, however, be guaranteed and factors which contribute to this conclusion include:

(a) the restricted accessibility of some fuel tank areas which has prevented adequate resealing;

(b) incomplete removal of degraded polyester from metal surfaces which leads to adhesion failures [4];

(c) less than satisfactory adhesion between the polysulfide seal and the epoxy barrier coat [3];

(d) the possibility that the epoxy adhesive may crack following vibration and flexing of the aircraft fuselage.

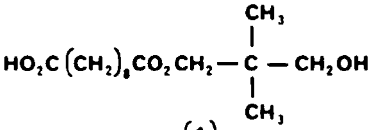
Although use of thick, broad fillet seals [2] would partly counter problems (b), (c) and (d), further repairs will probably be necessary.

There are indications that polysulfide sealants do not respond uniformly on contact with the polyester degradation products [2]. The possibility of a recurrence of fuel leaks has therefore prompted a detailed study of these interactions in an endeavour to rationalize the mechanisms involved and establish the relative resistance of various polysulfide sealants. Additionally, because the process impairs the performance of polysulfides it was conceivable that a new desealing approach could be identified. While the current method is efficient, the extended operating times, noxious thiol vapours which accompany the process, and problems of disposal of waste solutions [5] suggest that a clean, non-odorous procedure would be beneficial.

Prior to this examination the polyesters and their degradation products were characterized [6]. It was shown that both EC 5106 and EC 5146 were derived principally from sebacic acid and neopentyl glycol and that the most significant difference between the sealants was the greater proportion of trihydric alcohol incorporated in EC 5146 which permits a higher degree of crosslinking. In this report the consequences of contact between commonly used polysulfide fuel tank sealants (PR-1750, Pro-Seal 899 and PR-1422) and the hydrolysis products of the polyesters EC 5106 and EC 5146 are examined and discussed in relation to changes in the performance properties of the polysulfides.

2. RESULTS AND DISCUSSION

The consequences of contact between polyester degradation products and polysulfides was examined by (a) evaluation of the effect of model degradation products on the hardness, volume swell, flexibility and adhesion of various polysulfide sealants; (b) treatment of polysulfides with hydrolysis products of the polyester sealants EC 5106 and EC 5146 and monitoring the changes in various sealant properties; and (c) study of the performance of epoxy barrier, polyester and polysulfide systems in a simulated fuel tank structure.



$$HO_2C(CH_2)_8CO_2CH_2-\underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{\underset{|}{\overset{|}{C}}}}-CH_2OH$$

(1)

$HO_2C(CH_2)_8CO_2CH_3$

(2)

$HOCH_2CH_2NHCO(C_7H_{14})CONHCH_2CH_2OH$

(3)

$CH_3CH_2CONHC_2H_5$

(4)

2.1 *Effect of Model Degradation Products on Polysulfide Sealant Properties*

The possibility that particular polyester degradation fragments would have a selective and major effect on polysulfide sealants was examined using simulated degradation products. Although exhaustive hydrolysis of the polyesters would generate sebacic acid and neopentyl glycol, in practice ester units such as (1) which are terminated with both hydroxyl and carboxylic acid groups would be expected [6]. Methyl hydrogen sebacate (2) was selected as representative of such species. The proportion of amide groups in the polyester is not high and whereas complete degradation would produce the diamide (3) it has been shown that the amides will be retained in the main chain or as pendant branches [6]. Certain amides including dimethylformamide and pyrrolidone cause severe swelling of polysulfide sealants [5] and *N*-ethylpropionamide (4) was synthesised as a simple model of (3) in order to assess its likely influence on various polysulfides.

Specimens of polysulfide sealants were immersed in solutions of the model degradation products in dimethyl sebacate (Table 1) which were maintained at 60°. At intervals the volume swell, hardness and flexibility of the samples were assessed. The individual effects of the components (Table 1) were however, masked by that of dimethyl sebacate which, like other liquid polyesters, is a very effective plasticiser for rubbers and resins [7]. A second series of tests using ethanol gave the results shown in Table 2. The general effects of the individual components can be summarised as follows. Dimethyl sebacate was an effective swelling agent for the polysulfide sealants and produced volume swell of 180-300%. Under such conditions the sealant became too soft for hardness to be measured and after prolonged immersion one material, PR-1422, began to disintegrate. Contact with ethanol caused slight to moderate swelling and softening of the polysulfides with PR-1422 being the most susceptible. Neopentyl glycol suppressed the swelling due to dimethyl sebacate and this effect appeared greater than would be expected merely from dilution. In ethanol as solvent, however, the swell and hardness changes were insignificant. When used with dimethyl sebacate the diol also suppressed swelling considerably. A similar trend to that observed for dimethyl sebacate occurred with methyl hydrogen sebacate: swell of 20-40% was observed and the hardness, although reduced, was measurable. As the concentration of carboxylic acid was low its effect was generally masked but more significant changes were observed with solutions containing sebacic acid. Volume swell of the order of 30% resulted and was associated with the formation of a hard, inflexible coating on all sealants with PR-1750 and Pro-Seal 899 being the most brittle (Figure 2). The central core of the sealants, however, became considerably softened. When flexed, the brittle surfaces began to disintegrate and cracks of 0.5 to 1.0 mm in depth were produced. Little effect on the sealants occurred as a result of contact with N-ethylpropionamide. Initial contact produced surface tackiness but changes in hardness and swell were minor.

The only chemical reaction that appears to occur with these reagents is that between a polysulfide and the organic acids. Such processes have previously been proposed [8] to explain the embrittlement which results when polysulfides undergo prolonged heating. Acid catalysed hydrolysis of the formal group of the ethyl formal disulfide backbone produces formaldehyde (equation 1). This then acts to reduce polymer disulfide bonds generating formic acid (which catalyses further hydrolysis) and a thiol (equation 2). Further reactions may also occur as shown in equation 3. these processes lead to a weight loss and hardening of the polymer as a result of monosulfide formation. As flexibility occurs through rotation at the disulfide and formal groups, acid induced reactions which affect such groups will lead to stiffening and embrittlement of the sealant.

$$\sim SCH_2CH_2OCH_2OCH_2CH_2S\sim \; + \; H_2O \rightarrow \; \sim SCH_2CH_2OH \; + \; CH_2O \; + \; HOCH_2CH_2S\sim \tag{1}$$

$$\sim CH_2CH_2SSCH_2CH_2\sim \; + \; CH_2O \rightarrow 2 \sim CH_2CH_2SH \; + \; HCOOH \tag{2}$$

$$\sim CH_2CH_2SH \; + \; HOCH_2CH_2S\sim \; \rightarrow \; \sim CH_2CH_2SCH_2CH_2S\sim \; + \; H_2O \tag{3}$$

Of interest was the response of sealants to mixed reagents. Mixtures 5 and 7 which both contained sebacic acid and the diol in dimethyl sebacate did not immediately affect sealant hardness as markedly as the individual reagents. It was inferred that the diol suppressed swelling by the diester and allowed the hardening process due to contact with the diacid to proceed more effectively. In the case of Pro-Seal 899 this eventually resulted in an extremely brittle surface which immediately cracked when flexed.

Of the three polysulfides which were investigated, PR-1750 consistently displayed the greatest resistance to contact with the reagents. The remaining pair had similar volume swell in all mixtures. PR-1422 exhibited the least susceptibility to hardening by the diacid and was able to retain a reasonable degree of flexibility.

The different responses of the polysulfides to the ester solvents reflect the crosslink densities in the sealants. In a study of the swell of these polysulfides in hot water [9] it was found that each sealant was filled with calcium carbonate to approximately the same level. In addition, the ammonium dichromate curing agent used with PR-1422 was shown to be a more efficient oxidant of thiols than the manganese dioxide used to cure PR-1750 and Pro-Seal 899. This effect, however, is more than offset by the higher thiol content of the base polymers of PR-1750 and Pro-Seal 899 which leads to greater crosslink density in these sealants than in PR-1422. The volume swell results shown in Tables 1 and 2 are consistent with these conclusions and in each case a typical saturation curve is produced. The reasons for the better resistance of PR-1422 to embrittlement by acid are unclear. The observed behaviour is analogous to that which occurs on immersion of the three sealants in hot water: PR-1750 and Pro-Seal 899 undergo degradation under such conditions whereas PR-1422 is stable. A suggested explanation involves an initial autoxidation to produce an alkyl peroxide which subsequently decomposes with chain scission and it was concluded that such radical formation would be suppressed in the presence of chromium ions [9]. A similar effect could possibly operate in the reaction of the polysulfides with organic acids.

2.2 Effect of Degraded Polyester Mixtures on Polysulfide Sealants

Various approaches were used to assess the combined effect of degraded polyester sealant products on the polysulfides. Volume swell, hardness and flexibility were examined by immersing the cured polysulfides at 60° in the viscous resins obtained after removal of the fillers from EC 5106B (the prepolymer), hydrolysed EC 5106B and the degraded polyester sealant EC 5106. Further immersion studies were conducted with these polyesters in ethanol and using degraded EC 5146 sealant (with fillers). Results are shown in Table 3 and may be compared with those derived by Carroll and Pritchard [2] (Table 4). The variations are attributed to the use of different experimental conditions. The earlier data was obtained by curing the polyester around the polysulfide and then promoting degradation by maintaining the sample at 93° and 95% relative humidity. An over-aged curing agent was also used to prepare the EC 5106 and this affords a less cross-linked sealant that is highly susceptible to hydrolysis. In contrast, our polyester was degraded prior to contact with the polysulfides and interaction occurred at 60° in a dry atmosphere. We had previously observed that polysulfide sealants undergo substantial swell when immersed in hot water [9] and consequently the high humidity and temperature used in the General Dynamics investigation would be expected to influence the results. Although control samples were used in those studies (Table 4) the hardness changes are similar to those obtained at 90° in air (Table 5). Considerable swelling and softening was found to result from ageing the polysulfide sealants at 90° under high humidity (Table 5; Figures 3,4). The results obtained by Carroll and Pritchard are therefore not directly comparable.

Contact of polysulfides with degraded polyester sealants (Table 3) produced moderate swelling, which by reference to the model reagent effects may be attributed to both the ester and carboxylic acid groups. The drop in hardness was only marginal for the first 30 days, (control samples indicate some post-curing) but extended exposures showed that, although there is moderate swelling, similar hardening and embrittlement of the surfaces occur as with sebacic acid as reagent. Little difference in response was noted between EC 5106B and hydrolysed EC 5106B which suggests that the prepolymer was significantly hydrolysed before reaction [6]. The cores of sectioned samples were also noticeably soft relative to the surface hardness. Under such conditions the hardness measurements depend critically on the method and care used to remove the adhering polyester degradation materials as disruption of the brittle surface will lead to a low hardness result. In an attempt to avoid such problems, ethanolic solutions of the degraded polyester products were used. In these cases, however, the influence of the diluted reagents was masked by that of the solvent (Table 3).

Since good adhesion of fillet seals in aircraft fuel tanks is essential, the effect of residual polyester degradation products on the adhesion of polysulfides has been examined [4]. Peel tests were conducted on Pro-Seal 899 and PR-1422 which were applied over polyurethane coated panels covered with a thin film of degraded EC 5106. Although PR-1422 adhered better to the contaminated surface than did Pro-Seal 899, the values before conditioning were low and following immersion in jet reference fuel (JRF) all adhesion was lost. Stringent surface cleaning procedures are therefore important to ensure the removal of degraded materials from the desealed tanks prior to the resealing phase.

In terms of aircraft maintenance, however, the effect on sealant adhesion of several small, isolated leakages of polyester hydrolysis products is more relevant. A combination of chemical interaction, swell and expansion pressures conceivably could lead to reduced adhesion. It is not considered that such effects would be augmented by softening of the polysulfide through prolonged immersion in fuel [9,10] since the fuel temperatures would not be sufficient to lead to significant changes. In order to simulate the migration of degraded sealant into the interface between primed aircraft panels and the fillet sealant, a peel panel conforming to those specified in MIL-S-83430 was used with the modification shown in Figure 5. Half of the panel was perforated by an array of holes and these were filled with degraded polyester. The remaining half of the panel was used to provide reference data. The panels were conditioned either by immersion in JRF at 60°C or maintained at 90°C and 100% relative humidity.

No significant differences were noted in adhesion performance between the normal and modified sections of the panels (Table 6). In this approach the polyester did not undergo degradation *in situ* and consequently only the pressures resulting from thermal expansion would develop. Therefore, a considerable contact area between the polysulfide sealant and polyester degradation products appears necessary before separation of polysulfide contributes to the development of a fuel leak.

2.3 Fuel Tank Structures

To evaluate barrier coat materials for the F-111 reseal programme, Carroll and Pritchard [2] devised a test panel (Figures 6,7) which simulated sealed fuel tank faying surfaces. This has now been used to assess relative performance of polysulfide sealants in the presence of degraded polyester sealant. The aluminium alloy was protected with chromate conversion and corrosion prevention coatings as specified for F-111 fuel tank structure and voids were filled with degraded EC 5106. Various combinations of epoxy barrier coats (both EC 2216 and EC 3598) and MIL-S-83430 sealants were applied around the edges of the top plate and after these had cured the specimens were conditioned at 95° and 95% relative humidity. Periodically the panels were examined and changes were recorded photographically. During the ageing process, EC 5106 degradation products exuded from some grub screws, flowed to the edges of the specimen and initiated adhesion failures between the fillet seal and panel surface. All panels were then removed and the screws were resealed with EC 3598 to prevent further occurrences of this effect which was most prevalent when an epoxy barrier was present.

The different combinations examined by this procedure provide a guide to the effectiveness of resealing concepts. Originally two flexible epoxy adhesives were suggested for the F-111 refurbishment [2,3]. Of these, EC 3598 (a thickened version of the standard EC 2216) was developed for use on ceilings and vertical surfaces and it subsequently was selected as the approved barrier material. The intent of using broad fillets (Figure 7) in place of the normal type was to provide a safeguard in the event of a rupture of the barrier coat.

The performances of the various systems are summarised in Table 7, pertinent features are depicted in Figures 8-10, and the failure mode is illustrated in Figures 8 and 9. Onset of failure is characterized by a pronounced localized swelling which eventually erupts permitting discharge of degraded polyester materials. A similar sequence has also been noted on examination of F-111 fuselage fuel tanks. By probing the fillet seal with an indentor it was established that formation of the mounds was preceded by hardening of the polysulfide in contact with the polyester. The failure process may be rationalized in terms of an initial weakening of the polysulfide sealant matrix due to swell. Development of the mounds then follows as a result of expansion pressure from the confined polyester acting upon the softened polysulfide sealant. A combination of these effects will ultimately lead to rupture of the polysulfide. The influence of organic acids in hardening the polysulfide is considered to be of secondary importance but the cracking which results would also reduce the resistance of the fillets to external pressure.

Experimental limitations prevented the effect of expansion pressures being examined thoroughly. The polyesters EC 5106 and EC 5146 are now unavailable and consequently studies involving hydrolysis of the polyesters *in situ* were precluded. The pressures arising in the simulated fuel structure specimens are therefore considered to result simply from thermal expansion of the mobile degradation products. In practice this would be preceded by pressure arising from swell of the solid polyester. Exposure of EC 5146 at 90° and 100% relative humidity results in 12% volume swell before hydrolysis converts the material to a tacky mass, and immersion in water at 90° leads to 28% volume swell before a similar state is reached.

Examination of Table 7 indicates that the broad fillets provide substantially greater protection than do the normal sealant beads. This is interpreted in terms of a mechanical effect, since doubling the thickness will increase the bending stiffness by a factor of four and provide much greater resistance to expansion pressures. It is also apparent that of the sealants examined, PR-1750 is more resistant to rupture than Pro-Seal 899 either alone or in combination with the epoxy barriers (Figure 10). It is probable that the better performance of PR-1750 reflects the higher degree of cross-linking in this sealant relative to Pro-Seal 899. This leads to higher modulus and better swell resistance. No distinction in relative performance between the two epoxy materials could be discerned and as EC 3598 is more convenient to apply, its use in resealing was vindicated. The conditions of this experiment were severe relative to the typical service situation. The ability of the broad fillets of PR-1750 to perform satisfactorily, especially in the absence of the epoxy coat, was therefore encouraging. Indeed the value of the barrier could be debated for the case of broad fillets whereas if normal thickness fillets of PR-1750 or either thickness of the more susceptible Pro-Seal 899 were to be used the epoxy coat would need to be retained.

3. CONCLUSIONS

The formation of fuel leaks in F-111 integral tanks is a complex process. The consequences of contact between polysulfide sealants and reagents containing specific functional groups have been examined: ester fragments were shown to induce swelling, the alcohol groups in the degraded material suppress welling and the carboxylic acid groups both swell the sealant and harden the exposed surfaces. The secondary amide function appears to have little influence on the properties of the polysulfides.

The most obvious result of contact between polysulfides and degradation products of EC 5106 and EC 5146 was swelling which leads to a general softening of the sealant. This is accompanied, however, by some surface embrittlement and hardening. These effects alone would not produce a fuel leak and must be considered in conjunction with (a) the slight softening which results on prolonged contact of polysulfide sealants with fuel and (b) the pressures which result from the expansion of the polyester due to aerodynamic heating and swell in the presence of water vapour. A fillet sealant with such a greatly weakened matrix and a cracked surface would eventually rupture under the influence of the external pressures.

The performance of broad fillet coatings in providing extended protection to penetration by polyester degradation products emphasises the importance of maintaining this sealing practice throughout the lifetime of the F-111 aircraft. With this method the need to use a barrier coat is arguable, for the added protection of the epoxy material could be counteracted by the problems resulting from poorer adhesion between the barrier and the adjoining coats of polyurethane and polysulfide.

No obvious new desealing approach was identified as a result of this study. The value of using a powerful swelling agent in a desealing formulation was demonstrated by observing the effect of the sebacate ester on polysulfide polymers. Even at moderate temperatures, however, the degradation of polysulfides due to reaction with organic acids is very slow and therefore this effect cannot be incorporated into a practical desealing procedure.

4. EXPERIMENTAL

4.1 Materials

(a) Sealants and Coatings

The following polysulfide sealants were examined: Coast Pro-Seal 899 B-2, Products Research Corporation PR-1750 B-2 (both qualified to MIL-S-83430) and Products Research Corporation PR-1422 B-2 (qualified to MIL-S-8802E). Samples of 3M Company polyester sealants EC 5106 and EC 5146 were obtained through Air Office, Department of Defence. Sealants were cured by mixing the prepolymers EC 5106B and EC 5146B with the appropriate curing agent according to the manufacturer's directions. The polysulfides were mixed in a Semco pressure mixer model S-1350 in order to ensure uniform sample preparation. Aluminium panels were first treated with Dulux Industrial Chemicals Alodine 1200 chromate conversion coating and then Products Research Corporation polyurethane fuel tank coating PR-1560-MK (qualified to MIL-C-27725B) prior to application of sealant. The barrier coats used in the simulated fuel tank structure were 3M Company two part epoxy adhesives Scotchweld EC 2216 and EC 3598.

(b) Model Degradation Compounds

Methyl hydrogen sebacate (m.p. 37°) and dimethyl sebacate (m.p. 26°) were synthesised by fractional distillation of the product from the esterification of sebacic acid with methanol in the presence of c. hydrochloric acid as catalyst. *N*-ethylpropionamide was prepared from propionyl chloride and ethylamine [11] as a colourless liquid (b_3 84°). Neopentyl glycol (2,3-dimethyl-1,3-propanediol) and sebacic acid were obtained as analytical grade samples and were used without further purification.

(c) Degraded Polyester Mixtures

Samples of hydrolysed EC 5106 and EC 5146 prepolymers and sealants, freed from fillers, were obtained as previously described [6].

4.2 *Effect of Model Degradation Compounds on Polysulfides*

The polysulfide sealants were cured in a mould for 72 h at 25° and 50% RH, followed by 24 h at 60° and then a further 14 days at 25° and 50% RH. Duplicate discs (24 mm diam. x 6 mm thick) cut from the moulded sheet were immersed in sealed vials containing the solutions described in Tables 1 and 2, and then conditioned at 60°. At intervals measurements were taken of volume swell (procedure 10.1 of ASTM D471) and hardness (using Rex durometers, type A, models 1604 and 1700). The response of the samples to manual flexing through 60° was observed and the severity of cracking assessed subjectively in terms of the ability of the material to maintain a sealing function.

4.3 *Effect of Polyester Degradation Materials on Polysulfides*

(i) Duplicate discs of polysulfide sealant (19 mm diam. x 7 mm thick) were immersed in sealed vials containing ethanolic solutions (30% by weight) of polyester prepolymer, degraded polyester prepolymer and degraded polyester sealant. The specimens were conditioned at 60° and monitored periodically for changes in hardness, volume swell and flexibility.

(ii) Cured plugs of polysulfide sealants (9 mm diam. x 7 mm thick) were totally immersed in the following materials:

(a) degraded EC 5106 polyester sealant, without fillers;

(b) degraded EC 5146 polyester sealant, with fillers;

(c) EC 5106B prepolymer, without fillers;

(d) hydrolysed EC 5106B prepolymer, without fillers.

The samples were maintained at 60° and periodically were removed and cleaned (the final step being an ethanol wash combined with gentle wiping by tissue paper). Dried specimens were conditioned at 25°, 50% RH for 2 h before evaluation. Control specimens in sealed tubes were aged in an oven maintained at 60° ± 0.5°.

4.4 *Effect of Degraded Polyester on Polysulfide Adhesion*

Aluminium plates coated with PR-1560-MK polyurethane were used to prepare peel panels in accord with MIL-S-83430, clause 4.7.11, but with the following modification.

An array of 36 holes of 2 mm diameter was drilled over half the panel surface (see Figure 5). The rear face was then coated with polyethylene to provide a temporary filling in the apertures. This was achieved by placing the panel on a polyethylene sheet (1 mm thick), each side of the panel was then covered with teflon sheet and finally the sandwich was press moulded at 150° and 6.[illegible] MPa for 2 min.

Mixed polysulfide sealant was then applied to the front face of the panel and the peel specimen was developed in the normal manner. After the sealant had cured the polyethylene was peeled from the rear surface and the apertures. The area in the vicinity of the holes was washed with trichloroethylene and degraded EC 5146 polyester was injected into the apertures by syringe. A coating of EC 2216 epoxy adhesive was applied over the apertures to contain the polyester and then an outer layer of PR-1422 B-2 to protect the epoxy from jet reference fuel (JRF).

The panels were immersed in JRF at 60° and the peel strength determined at intervals, according to MIL-S-83430, 4.7.11. Prior to measurement of peel strength the panels were conditioned at 25° and 50% RH for 2 h. At all sampling intervals reference measurements were obtained from the unmodified section of each panel. Additional specimens were prepared, exposed at 90° and 95% relative humidity and the peel strengths similarly determined at various intervals.

4.5 Relative Performance of Polysulfides in Simulated Fuel Tank Structures

A structure which simulates the sealed faying surfaces, injection holes and structural voids of a fuel tank was constructed of polyurethane-coated aluminium alloy panels (Figure 6) [2]. Degraded EC 5106 polyester sealant was introduced into the voids between the upper and lower plates which were then bolted together and grub screws inserted in the injection holes. Various combinations of epoxy barrier coats and polysulfide sealants in both normal or broad fillets (see Figures 7-10) were then applied around the sides of the panels. The cross-section of the normal fillet formed a right-angled triangle (Figure 7) with a base of 5 mm. The broad fillets had a base of 10-12 mm and the profile of the upper surface was slightly convex. Sufficient panels were used to provide quadruplicates of each combination of materials. After standard cure the specimens were placed on their sides in desiccators containing saturated K_2SO_4 solution (which provided a relative humidity of 95%) and these were maintained in an oven at 95°. The panels were examined regularly for changes in fillet configuration and a photographic record was maintained. With time, polyester degradation products exuded from the grub screws and flowed down the plates eventually contacting the polysulfide fillets. To prevent this effect, the grub screws were sealed externally with epoxy adhesive. This was carried out on all panels which were still in satisfactory condition after 35 days.

4.6 Effect of Humidity on Volume Swell and Hardness of Polysulfide Sealants

Discs of sealant (19 mm diam. x 7 mm thick) were maintained in a fixed environment of 90° and 100% relative humidity. Control samples were evaluated simultaneously by storing the sealant discs at 90° in a sealed dry tube within the same cabinet. The sealant discs were removed periodically and changes in volume swell and hardness were recorded.

4.7 *Volume Swell of EC 5146 Sealant*

Cured plugs of EC 5146 (initial Rex A hardness 74) were either immersed in distilled water maintained at 90°, or exposed in air at 90° and 100% relative humidity. Volume swell was determined according to ASTM D471 over 11 days by which time the sealant had become too soft for hardness measurements to be taken.

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TABLE 1

EFFECT OF SOLUTIONS OF MODEL DEGRADATION PRODUCTS IN DIMETHYL SEBACATE ON PROPERTIES OF POLYSULFIDE SEALANTS

A. VOLUME SWELL (%)

MIXTURE[a]	IMMERSION TIME (DAYS)								
	PR-1422			Pro-Seal 899			PR-1750		
	7	12	19	7	12	19	7	12	19
1	227	282	371	178	238	269	140	181	195
2	207	240	262	161	199	226	130	154	163
3	62	67	83	50	55	62	42	44	47
4	113	175	227	127	135	166	93	101	107
5	35	46	65	43	46	46	37	43	47
6	119	180	231	120	126	142	95	103	109
7	37	52	61	42	42	46	37	45	48

B. HARDNESS[b]

MIXTURE[a]	IMMERSION TIME (DAYS)							
	PR-1422 (64)			Pro-Seal 899 (45)			PR-1750(55)	
	12	19	26	7	12	19	12	19
1	c	c	c	c	c	c	c	c
2	c	c	c	c	c	15	10	21
3	7	7	13	c	5	9	12	9
4	c	3	c	c	4	4	16	22
5	31	22	8	39	43	88	40	51
6	5	c	c	5	11	13	19	20
7	29	26	54	33	57	88	51	57

TABLE 1 Contd.

C. PHYSICAL CONDITION AFTER 19 DAYS

MIXTURE[a]	FLEXIBILITY			PHYSICAL STATE			EFFECTIVENESS AS SEALANT		
	PR-1422	Pro-Seal 899	PR-1750	PR-1422	Pro-Seal 899	PR-1750	PR-1422	Pro-Seal 899	PR-1750
1	moderate	high	high	d	good	good	poor	good	good
2	low	moderate	moderate	d	d	brittle	poor	poor	poor
3	high	high	high	good	good	good	good	good	good
4	high	moderate	high	good	brittle	brittle	good	poor	good
5	high	low	high	good	brittle	good	good	poor	good
6	high	moderate	high	good	brittle	good	good	poor	good
7	low	low	low	brittle	brittle	brittle	poor	poor	poor

[a] Compositions (v/v) in dimethyl sebacate : 1,dimethyl sebacate (100%); 2, sebacic acid (17%); 3, neopentyl glycol (30%); 4,methyl hydrogen sebacate (17%); 5,sebacic acid (12%), neopentyl glycol (25%); 6,sebacic acid (15%), methyl hydrogen sebacate (15%); 7,sebacic acid (11%), neopentyl glycol (22%), methyl hydrogen sebacate (11%).

[b] Original hardness given in parentheses

[c] Material too soft to measure

[d] Disintegrating

TABLE 2

EFFECT OF ETHANOLIC SOLUTIONS OF MODEL DEGRADATION PRODUCTS ON PROPERTIES OF POLYSULFIDE SEALANTS

A. VOLUME SWELL (%)

MIXTURE[a,b]	IMMERSION TIME (DAYS)											
	PR-1422				Pro-Seal 899				PR-1750			
	6	14	28	42	6	14	28	42	6	14	28	42
8	7	8	8	8	4	6	7	10	4	4	5	5
9	7	7	8	8	4	5	7	7	3	3	3	3
10	13	18	29	30	11	15	20	25	6	11	16	20
11	14	23	34	46	15	23	36	42	11	16	23	26
12	21	30	39	39	15	20	22	24	8	11	15	18
13	1	c	c	c	0.6	c	c	c	0.2	c	c	c
Ref. (Air, 60°)	0.3	-0.7	-0.5	-0.4	0.4	-2.1	-2.9	-3.0	0.6	-1.3	-1.0	-1.7

B. HARDNESS[d]

MIXTURE[a,b]	IMMERSION TIME (DAYS)											
	PR-1422 (63)				Pro-Seal 899 (46)				PR-1750 (54)			
	6	28	60	180	6	28	60	180	6	28	60	180
8	59	51	47	46	44	44	41	35	53	52	50	46
9	59	57	53	54	46	45	43	35	52	51	50	46
10	58	46	35[e]	44[f]	65	76[g]	81[g]	86[g]	63	67[g]	76[g]	79[g]
11	49	42	38	33	42	36	26	25	49	46	38	38
12	44	41	37	34	36	36	27	24	41	41	36	33
13	h	50	44	37	h	37	34	31	h	44	42	41
Ref. (Air, 60°)	66	68	60		42	49	48		54	58	53	

[a] Compositions (v/v) in ethanol : 8,ethanol (100%); 9,neopentyl glycol (12%); 10,sebacic acid (25%); 11,methyl hydrogen sebacate (25%); 12,dimethyl sebacate (25%); 13,*N*-ethylpropionamide (12%).

[b] Other than the swelling and softening that occurs with some mixtures, the physical condition of the sealants was good except for the sebacic acid cases. Here all surfaces became brittle and the inner core was soft. PR-1750 and PR-1422 also developed surface tackiness subsequent to embrittlement.

[c] Change insignificant.

[d] Original hardness given in parentheses.

[e] Elastomeric but becoming spongy.

[f] Granular, porous surface which cracked on flexing but still retained some elasticity.

[g] Hard, brittle surface, cracks 0.5 - 1 mm deep on flexing, centre had softened.

[h] Surface tacky.

TABLE 3

EFFECT OF DEGRADED POLYESTERS ON POLYSULFIDE SEALANT PROPERTIES

A. VOLUME SWELL (%)

REAGENT	IMMERSION TIME (DAYS)														
	PR-1422					Pro-Seal 899					PR-1750				
	4	8	18	35	65	4	8	18	35	65	4	8	18	35	65
EC 5146 (D)	4	6	9	-	18	2	3	5	-	13	1	2	10	-	11
EC 5106B	2	4	9	13	16	0	0	2	6	11	0	1	3	7	10
EC 5106B (D)	5	7	12	17	20	3	4	9	11	15	3	3	6	9	12
EC 5106 (D)	3	5	8	13	16	0.1	0.1	1	4	10	0	1	1	3	6
Ethanol	6	8	9	11	12	4	5	6	7	9	3	4	5	6	6
EC 5106B/EtOH	10	10	11	13	18	6	7	8	10	11	5	5	6	7	6
EC 5106B (D)/EtOH	11	12	14	19	39	8	9	13	16	23	7	7	10	13	19
EC 5106 (D)/EtOH	10	10	11	14	24	7	6	7	10	17	6	5	6	6	7

D = Degraded sample

TABLE 3 Contd.

B. HARDNESS

REAGENT	IMMERSION TIME (DAYS)														
	PR-1422					Pro-Seal 899					PR-1750				
	0	4	18	35	85	0	4	18	35	85	0	4	18	35	85
Air (60°)	67	65	67	66	60	42	41	46	48	47	53	54	56	56	52
EC 5146 (D)	72	68	67	-	72	48	50	59	-	65	57	59	60	-	75
EC 5106B	68	63	61	62	62	44	43	49	49	55	53	52	55	60	63
EC 5106B (D)	67	62	62	63	64	43	42	50	53	58	53	53	61	60	67
EC 5106 (D)	68	65	66	60	63	44	44	49	47	53	52	53	52	51	58
Ethanol	66	60	50	48	43	42	38	36	35	29	51	43	44	43	40
EC 5106B/EtOH	66	47	50	48	40	41	33	33	32	25	50	42	42	41	32
EC 5106B (D)/EtOH	66	51	48	43	38	42	33	33	34	14	51	44	39	39	24
EC 5106 (D)/EtOH	65	51	47	46	38	43	30	34	25	21	52	41	43	35	34

D = Degraded sample

TABLE 4

CHANGES IN PROPERTIES OF POLYSULFIDES AFTER CONTACT WITH DEGRADED EC 5106 SEALANT [2]

PROPERTY	CONTACT TIME (DAYS)[a]					
	PR-1750			Pro-Seal 899		
	10	30	60	10	30	60
Hardness:						
Control	55	61	52	47	50	46
Sealant + EC 5106	52	51	46	40	38	36
Volume Swell (%)[b]			15			44

[a] Conditions : 93°, 95% relative humidity

[b] Measured as change in thickness of sample

TABLE 5

EFFECT OF HIGH HUMIDITY ON POLYSULFIDES

PROPERTY	EXPOSURE TIME (DAYS AT 90°, 100% RH)														
	PR-1422					Pro-Seal 899					PR-1750				
	0	8	18	35	85	0	8	18	35	85	0	8	18	35	85
Volume Swell (%)	0	3	10	12	39	0	3	14	29	52	0	5	16	24	73
Control[a]	0	-1.8	-1.3	-1.7	-2.3	0	-3.0	-4.0	-5.3	-6.7	0	-2.7	-3.5	-4.9	-6.4
Hardness	65	54	45	42	28	42	40	37	26	10	51	42	38	29	11
Control[a]	67	69	68	65	56	43	50	52	50	45	50	55	54	51	46

[a] 90°C, <5% relative humidity

TABLE 6

PEEL AND ADHESION PERFORMANCE OF POLYSULFIDE SEALANTS IN CONTACT WITH DEGRADED POLYESTER

A. IMMERSION IN JRF AT 60°

EXPOSURE TIME (hr)	PEEL STRENGTH (Kg/2.5 cm)					
	Pro-Seal 899		PR-1422		PR-1750	
	Normal	Modified	Normal	Modified	Normal	Modified
0	16	15	8	7	9	7
24	12^{a}	13^{a}	5^{b}	5^{b}	$3^{b,c}$	$3^{b,c}$
74	16^{a}	15^{a}	7^{b}	7^{b}	3^{b}	8^{c}
117	11^{a}	12^{a}	5^{b}	5^{b}	1^{c}	1^{c}
186	9^{a}	6^{b}	6^{b}	6^{a}	8^{a}	$5^{b,c}$
544	8	8	8	8	7^{b}	6^{b}

B. EXPOSURE AT 90° AND 95% RELATIVE HUMIDITY

EXPOSURE TIME (hr)	PEEL STRENGTH (Kg/2.5 cm)					
	Pro-Seal 899		PR-1422		PR-1750	
	Normal	Modified	Normal	Modified	Normal	Modified
0	16	15	8	7	9	7
24	22^{a}	21^{a}	12^{a}	12^{a}	16^{a}	16^{a}
74	16	15	14	14	10	13
186	3^{c}	3^{c}	8^{b}	8^{a}	4^{d}	2^{c}
290	3^{c}	$5^{b,c}$	10^{a}	10^{a}	4^{c}	$6^{b,c}$
426	2^{c}	3^{c}	3^{d}	6^{d}	4^{c}	4^{c}
544	3^{c}	2^{c}	10^{d}	9^{d}	2^{d}	3^{d}
1240	4^{c}	5^{c}	13^{a}	12^{a}	3^{c}	4^{c}

[a] Cohesive failure;

[b] Mesh peeled from sealant;

[c] Adhesive failure at panel surface;

[d] Mixed adhesive and cohesive failure resulting in a film of sealant adhering to panel.

Notes: (1) In some cases differences in failure modes occurred in the same panel following successive cuts.

(2) The minimum requirement for peel in MIL-S-83430 is 9.0 Kg/2.5 cm.

TABLE 7

DAYS TO FAILURE OF VARIOUS SEALING COMBINATIONS IN MODEL FUEL TANK STRUCTURES

SEALANT	NORMAL FILLETS			BROAD FILLETS		
	EPOXY COAT			EPOXY COAT		
	NIL	EC 3598	EC 2216	NIL	EC 3598	EC 2216
Pro-Seal 899	17	30	≈36[a]	30	57	75
PR-1750	57	57	>45[b]	>94[b]	75	105

[a] Results masked by leakage from around grub screws

[b] Experiment terminated at this point

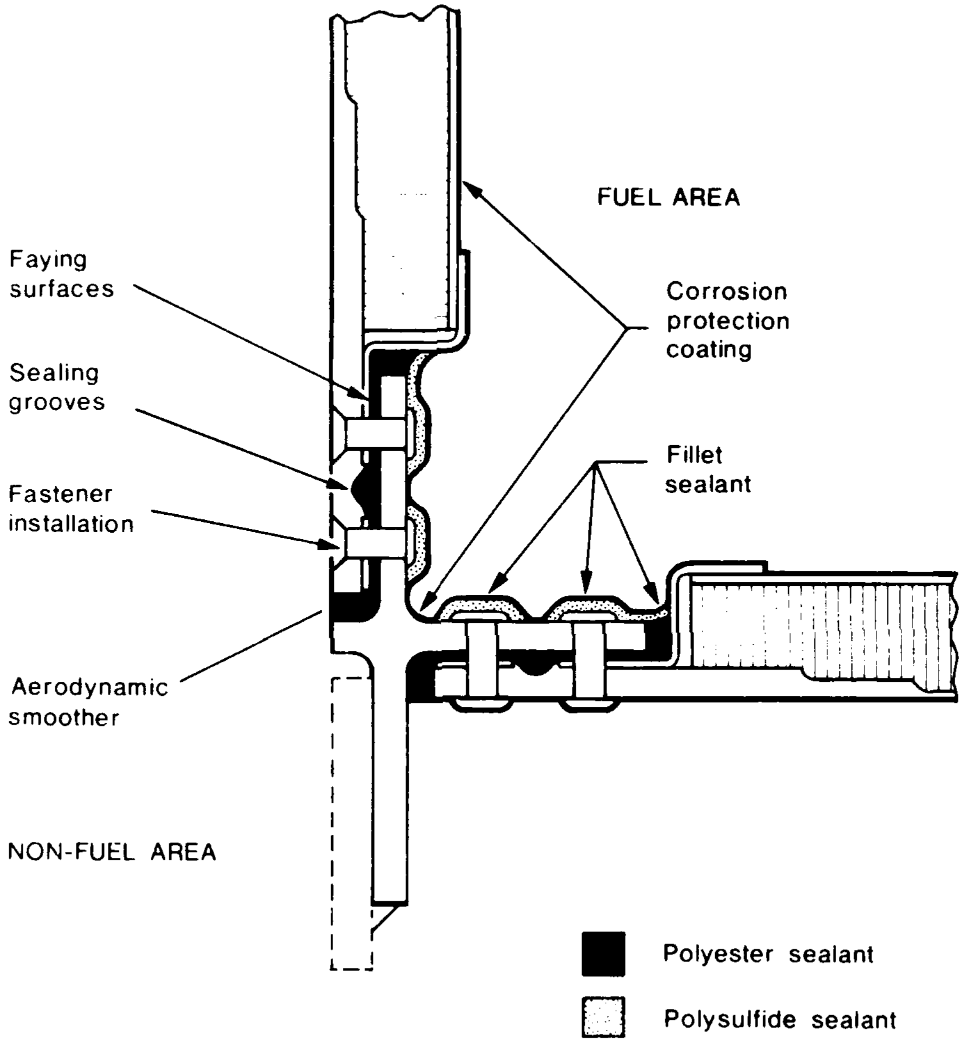

Figure 1. Multiple barrier sealing system in the F-111 fuselage fuel tank.

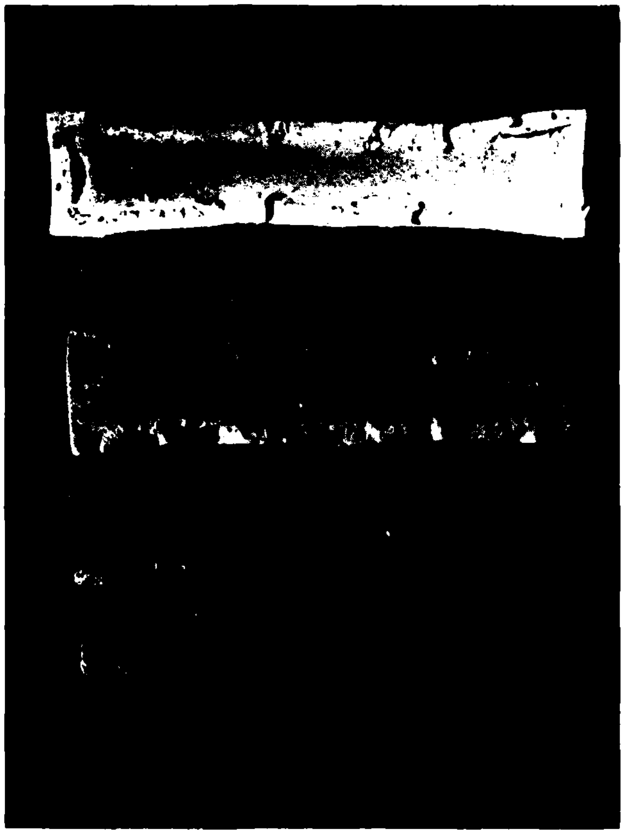

Figure 2. Cross section of polysulfide sealants following immersion for 180 days in a 1M ethanolic solution of sebacic acid at 60°; top: Pro-Seal 899, middle: PR-1750, bottom: PR-1422. Specimens were examined as discs of diameter 24 mm and thickness 6 mm. Surface hardened zones and cracking in PR-1750 and Pro-Seal 899 are evident whereas PR-1422 is less affected.

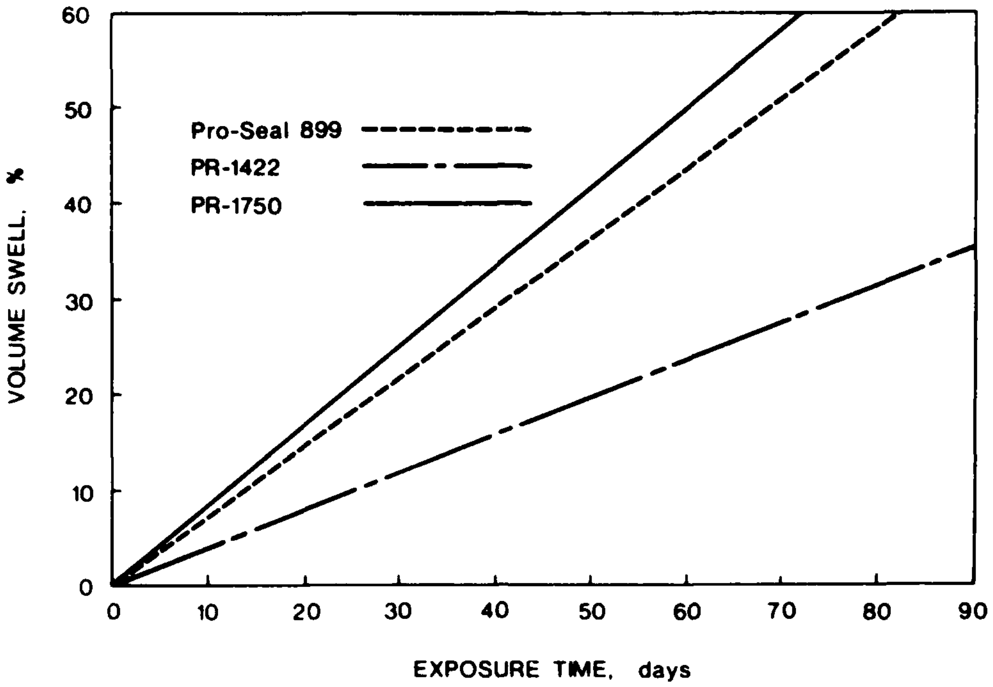

Figure 3. Changes in volume swell of polysulfide sealants after conditioning at 90° and 100% relative humidity.

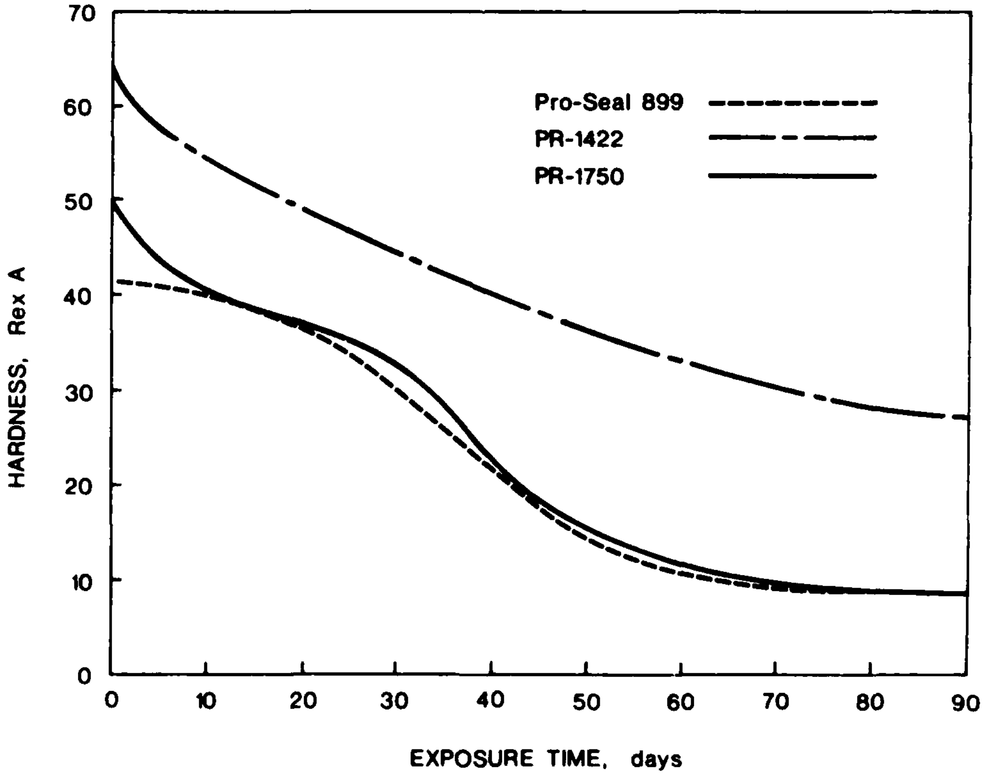

Figure 4. Effect of conditioning at 90° and 100% relative humidity on the hardness of polysulfide sealants.

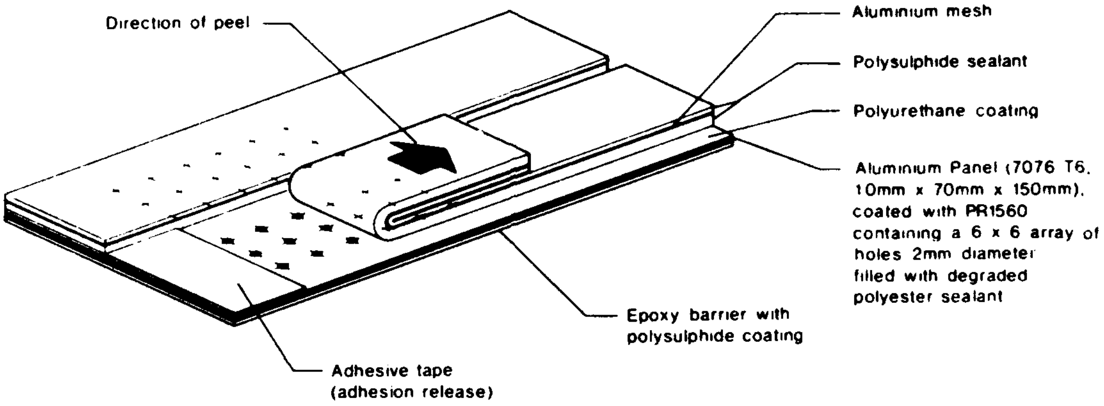

Figure 5. Modified peel panel for assessment of the effect of degraded polyester on the adhesion of polysulfide sealants.

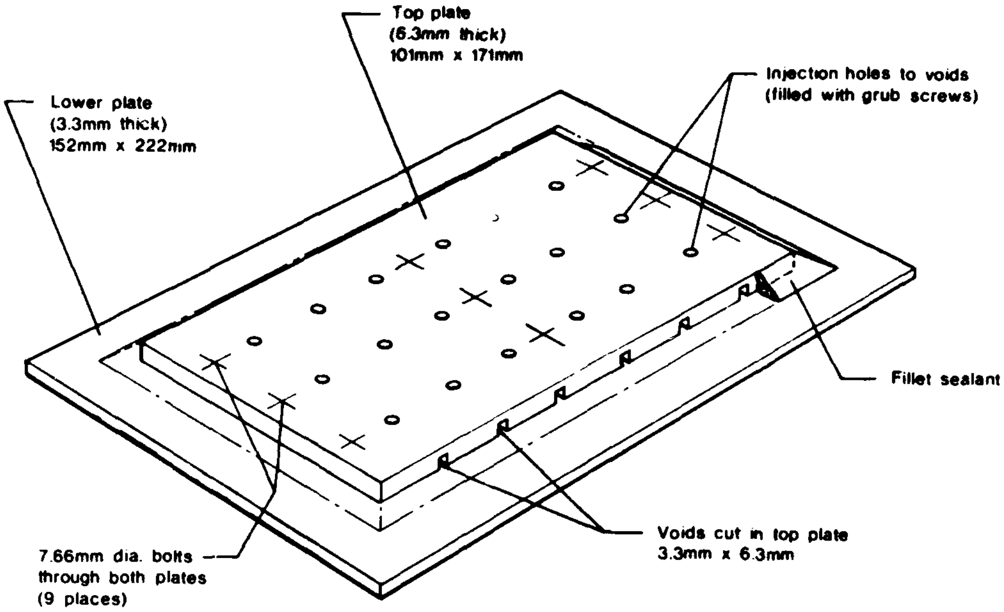

Figure 6. Simulated fuel tank structure used for determination of the relative effectiveness of barrier seals.

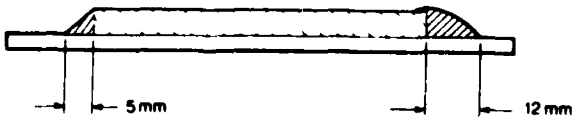

Figure 7. Normal and broad fillets applied to simulated fuel tank structure.

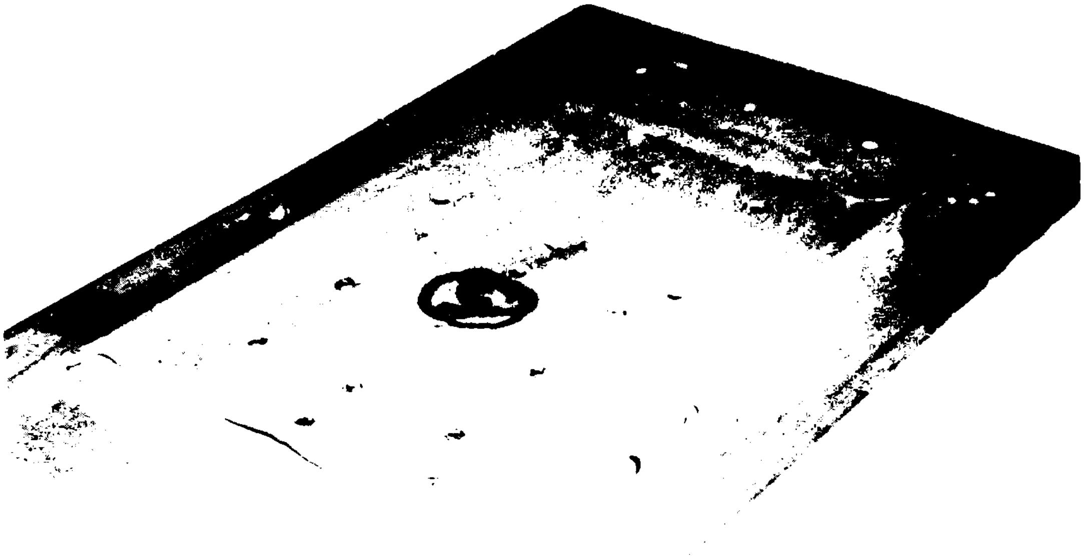

Figure 8(a)

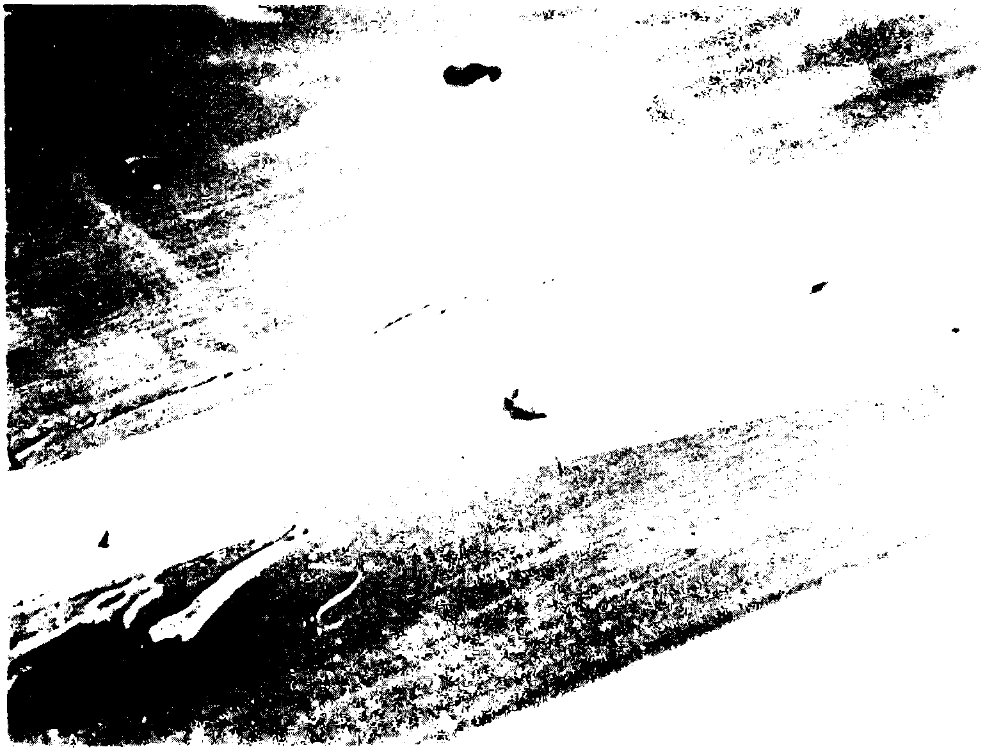

Figure 8(b)

Figure 8. Comparison of effectiveness of normal and broad fillet seals of Pro-Seal 899 (no barrier adhesive): (a,b) normal fillet, 7 days (c) normal fillet, 25 days (d) broad fillet, 7 days (e,f) broad fillet, 31 days.

Figure 8(c)

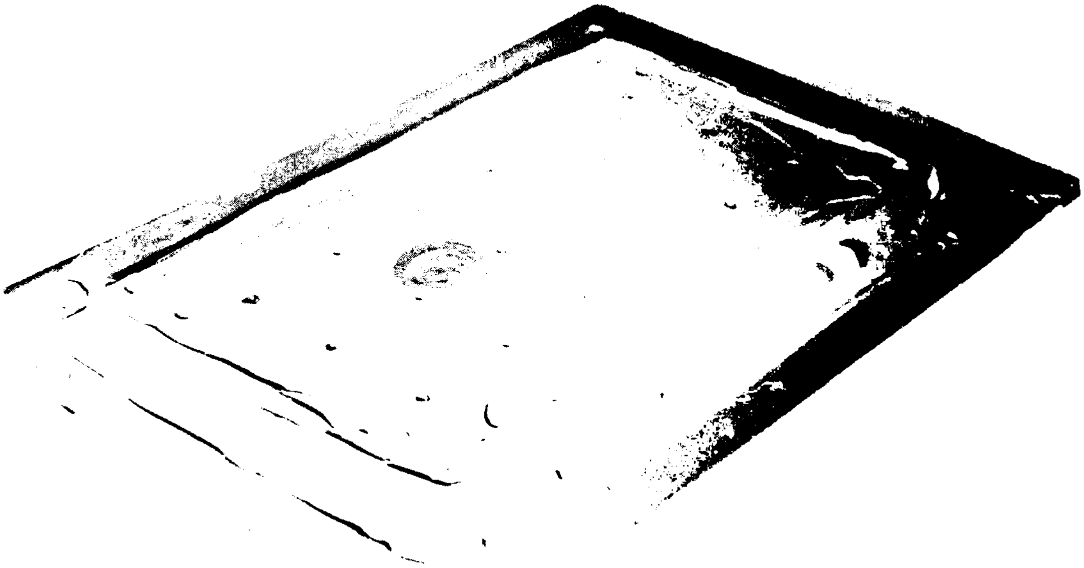

Figure 8(d)

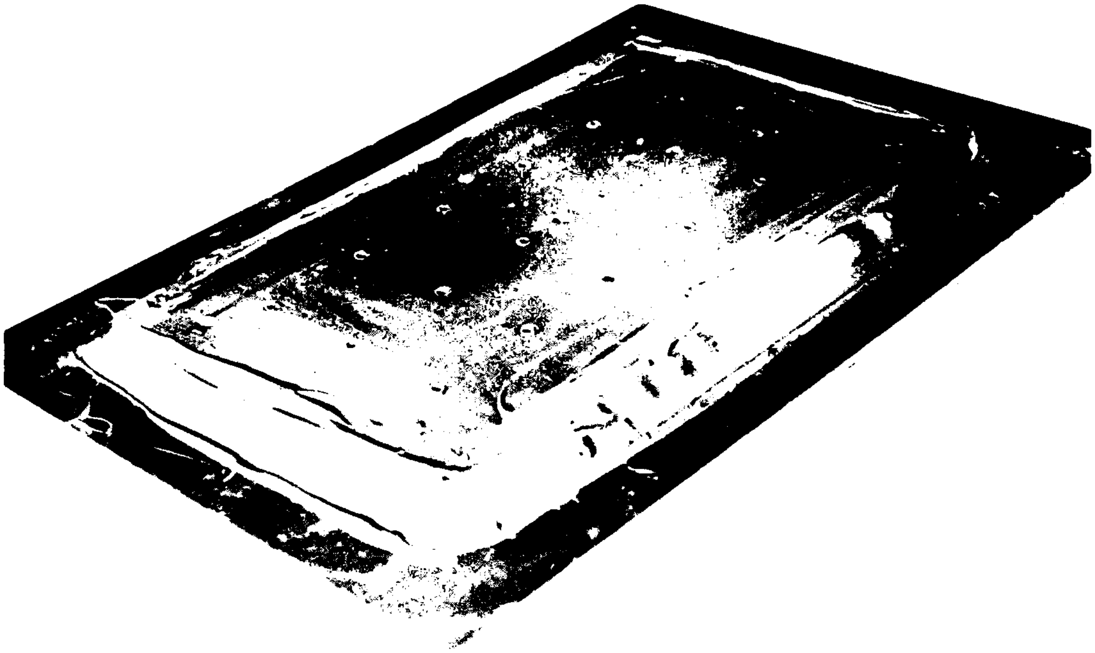

Figure 8(e)

Figure 8(f)

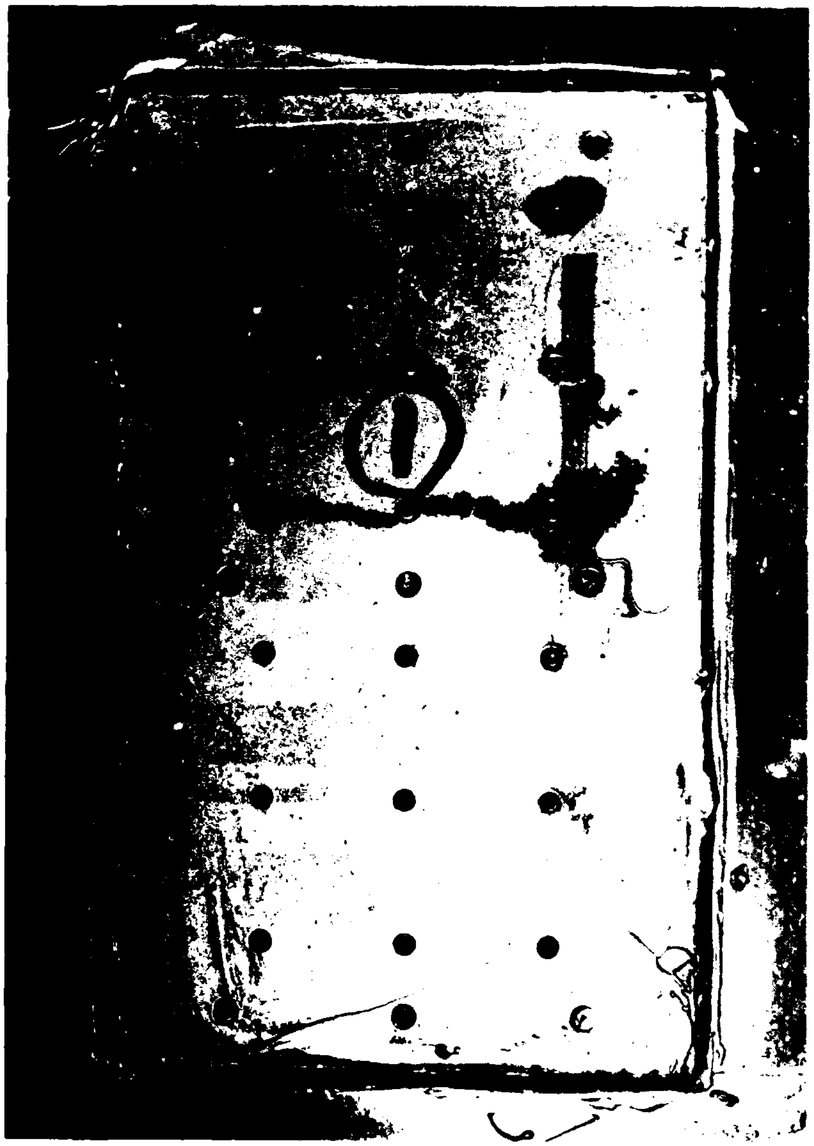

Figure 9. Effect of using barrier adhesive EC 3598 with normal fillets of Pro-Seal 899 - failure at 41 days (compare with Figure 8 (b)).

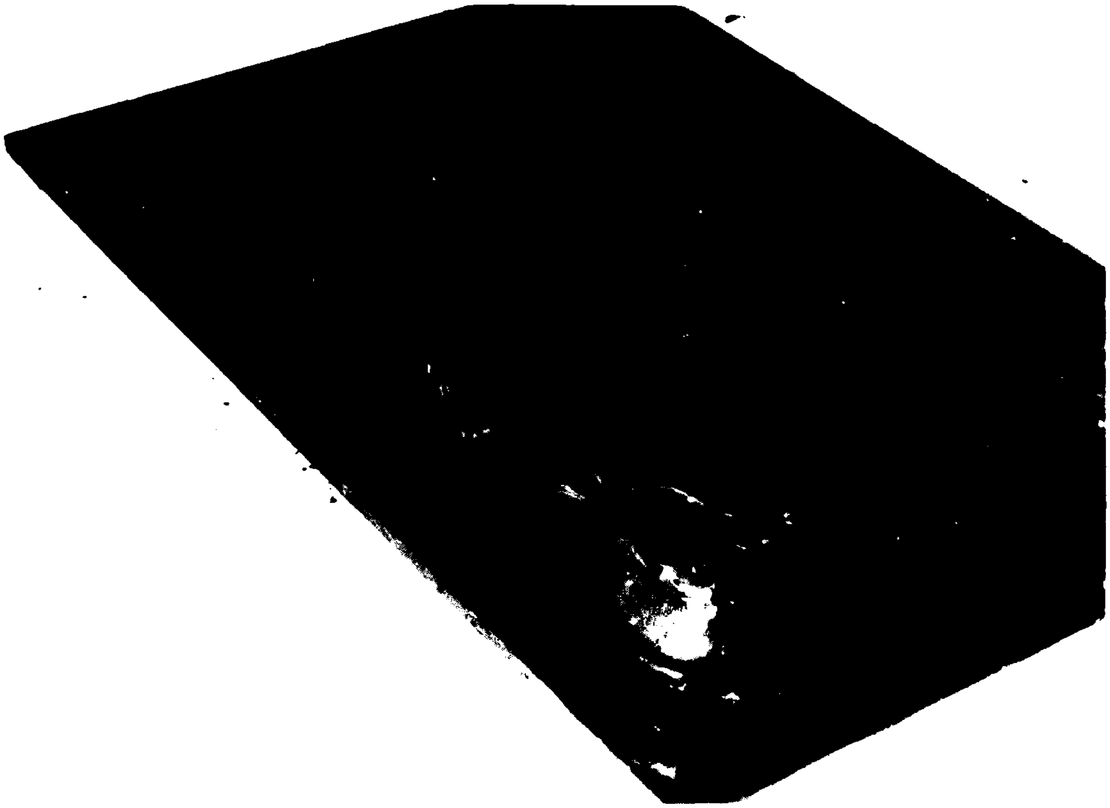

Figure 10. Panel sealed with broad fillets of PR-1750 (no adhesive barrier) after 94 days.

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