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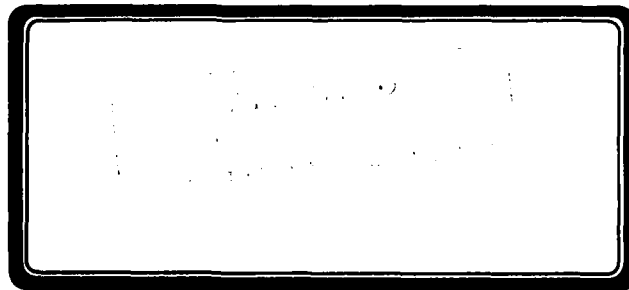
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Effect of temperature on the storage life of
polysulfide aircraft sealants

J.W. Barber, P.J. Hanhela, R.H.E. Huang and D.B. Paul

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**EFFECT OF TEMPERATURE ON THE STORAGE LIFE OF
POLYSULFIDE AIRCRAFT SEALANTS**

John W. Barber, Peter J. Hanhela, Robert M.E. Huang and D. Brenton Paul

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ABSTRACT

The storage performance of a range of PR-1422, PR-1436G and PR-1750 two-part polysulfide aircraft sealants of A and B classes, packaged both in cans and Semkit form, has been surveyed. The sealants were separately maintained at temperatures of -16°, 2°, 13° and 25° C and changes in viscosity of the polymer base compound, cure rate, peel strength and application life were monitored over 26 months. Concurrent changes in thiol content of the liquid polymer in the base compound and concentrations of Mn(IV) or Cr(VI) in the cure pastes were also determined. Variations in activity of cure pastes with time were assessed using LP-32 as a standard polymer and changes in polymer base compounds were monitored by measuring cure rate with laboratory prepared reference cure pastes.

Low temperature storage extended storage life significantly. After maintenance at temperatures of 2° C and below, the canned sealants still performed satisfactorily after two to three years storage. Most materials were procured several months after manufacture and with reduction of acquisition time further extension of the low temperature storage life could be expected. No significant storage differences between PR-1750 and PR-1422 sealants or the A or B classes were noted. Dichromate-based cure pastes were prone to lose solvent at higher storage temperatures and some dried pastes resulted. The main cause of failures was oxidation of the polymer base compound which led to surface skinning and was accompanied by a gradual drop in thiol content. Peel strength was unaffected by storage and the concentrations of Mn(IV) and Cr(VI) were little changed.

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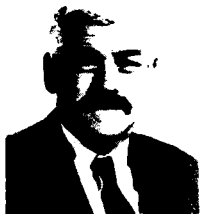
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EFFECT OF TEMPERATURE ON THE STORAGE LIFE OF POLYSULFIDE AIRCRAFT SEALANTS

1. INTRODUCTION

Polysulfide sealants derived from Thiokol liquid polymers are widely used in aircraft for sealing of integral fuel tanks, water tanks and crew modules, for aerodynamic smoothing and the formation of gaskets for hatch covers. There is a frequent requirement to replace sealants due to fuel or air leaks, rework or reinstallation of sealed equipment and materials must therefore be continuously available to meet such demands. The components of two-part polysulfide sealants are not indefinitely stable, however, and are supplied with the stipulation that performance properties cannot be guaranteed after a stated storage period at 27°C. For construction sealants this is generally 9 to 12 months but the stringent requirements of aircraft sealants reduce the recommended storage life to 6 to 9 months.

Local manufacture of aircraft sealants is mainly limited to the compounding of the dichromate-cured PR-1422 range by Selleys Chemical Company* under licence to Products Research Corporation although some batches of the manganese dioxide-cured PR-1750 sealants have also been produced. A proportion of sealants used on Australian aircraft are procured from USA and the long delivery route, in conjunction with delays due to customs and quality assurance approvals can reduce the remaining storage life to trivial periods. In addition there are no provisions to control the temperature of these materials when in transit. As a consequence significant quantities of time-expired or otherwise unacceptable sealants have been discarded annually by RAAF. Any modification to storage conditions which extends sealant shelf-life would be highly beneficial since procurement could be adjusted to accommodate fewer but larger orders resulting in more regular supply, reduced wastage and easing of quality control pressures.

Since polysulfide liquid polymers are reactive materials the instability of the sealant components is likely to result from chemical rather than physical effects. Any assessments of chemical reactivity, however, must involve consideration of the total sealant formulation which can entail such components as plasticizers, fillers, dispersants, cure rate modifiers, adhesion enhancers and viscosity

* Following the acquisition of Selleys Chemical Company by ICI Australia Ltd, sealant manufacture is now conducted by the Adhesives Division of ICI Operations Ltd.

adjusters in addition to the liquid polysulfide and curing agent [1-7]. Generally these additives are chemically inert but some components, particularly adhesion additives such as phenolic and epoxy resins, can participate in reactions which result in modified sealant performance. Recently we reported procedures to ascertain the compositions of several commercial two-part polysulfide aircraft sealants. In particular it was shown that conceivable interactions between the polysulfide thiol end groups and a phenolic resin adhesion additive, which could occur in the polymer base compound of a commercial formulation, do not proceed even after ageing at elevated temperatures [8].

The reactive centres of liquid polysulfides (1) are the formal groups in the polymer backbone and thiol terminal groups. Under normal conditions the disulfide linkages are stable both to oxidation and heat; low molecular weight aliphatic disulfides can be distilled unchanged at 200°C at atmospheric pressure [9]. The formal groups in the polysulfide structure, however, are susceptible to autoxidation and also hydrolysis [9-13]. The latter reaction requires acid catalysis and thermal degradation of liquid polymers at 100-150°C initially involves a free radical autoxidation to generate an organic acid before the hydrolysis proceeds.

The thiol terminal groups in polysulfides are involved in the oxidative cures used to produce sealants. They are also susceptible to air oxidation and under some circumstances curing can be achieved in this manner [4]. The curing systems for aircraft sealants are of the oxidative type and are based [8] on either manganese dioxide or dichromate salts (ammonium, calcium or magnesium). The stability of such materials with long term storage is not known, but slow oxidation-reduction reactions with other components such as dispersing oils, solvents, fillers, accelerators or retarders could result in reduced curing activity. Potential problems with solvents such as dimethylformamide or phthalate plasticisers have been recognised [4,8,14].

Although it is reasonable to conclude that the storage life of sealant components will be temperature dependent, product data sheets do not contain information on the effect of lowering storage temperature. Confidence that improved storage lives can be achieved at temperatures below ambient was provided, however, from a study of low temperature storage of pre-mixed sealants: after several months at -40°C most polysulfide sealants underwent virtually no change in performance properties [15]. A comprehensive program has therefore been undertaken to evaluate the influence of temperature on critical properties of various classes of the sealants PR-1422, PR-1750 and PR-1436G, stored at -16°C, 2°, 13° and 25°C. Both of the principal types of sealant packaging systems, cans and Semkits, were examined and effects were monitored over periods of up to three years in order to establish useful shelf lives under the various conditions. Spectroscopic and chemical examinations were also undertaken to relate any regular variations in performance which occurred during ageing to changes in measurable characteristics.

2. EXPERIMENTAL

2.1 Materials and Equipment

The sealants investigated were PR-1750 A-1/2, A-2, B-1/2, B-2 and B-6 (qualified to MIL-S-83430), PR-1422 A-1/2, A-2, B-1/2, B-2 and B-6 (qualified to MIL S-8802) in both cans and Semkits and PR-1436G, B-2 (qualified to MIL-S-81733) in cans only. All

were obtained either from Products Research and Chemical Corporation, Los Angeles, USA or Selleys Chemical Company, Sydney, Australia.

For cure rate studies LP-32 (Thiokol) was used as the reference polysulfide polymer and the laboratory prepared curing agents [12,16] were

- (a) a solution of ammonium dichromate (BDH; 1.0 g) in dimethylformamide (Ajax; 3.5 g) and water (0.1 g) and
- (b) a paste (1 : 1 w/w) of manganese dioxide (Riedel-de Haën, Type C) and di(2 ethylhexyl) phthalate (CSR Chemicals Corflex 810).

Peel tests were conducted using an Instron 1026 testing machine, viscosities were determined with a Brookfield Model RVF viscometer and hardness readings were assessed with a Shore A2 maximum reading durometer attached to a Conveloader, all in accordance with the appropriate military specification. Infrared analyses were obtained with a Perkin-Elmer 580B double beam, ratio-recording instrument equipped with a model 3600 data station and associated software.

2.2 Storage and Mixing of Sealant Components and Reference Materials

Separate containers of the unmixed polymer base compounds and cure pastes were maintained at temperatures of $25 \pm 2^\circ\text{C}$, $13 \pm 2^\circ\text{C}$, $2 \pm 2^\circ\text{C}$ and $-16 \pm 2^\circ\text{C}$. The sealant components were periodically removed and allowed to equilibrate at 25°C for one day before evaluation. A stainless steel stirrer blade with a horizontal impeller and two vertical blades was used in the mechanical mixing of components to ensure thorough blending and minimum entrapment of air. The mixed sealant was transferred into polyethylene cartridges (70 g, 2.5 oz) for dispensing by a Semco Model 250 sealant gun. Samples were tested at the outset of the program to determine compliance with specifications and the degree of tolerance of the batch within the individual requirements.

For each sample, small quantities of the unmixed components were retained and stored at -20°C to subsequently assess any changes in chemical composition and cure rate with reference components which were freshly prepared as needed.

2.3 Physical Testing

At selected intervals matching commercial sealant samples were withdrawn from the various storage conditions and assessed [15] against requirements for tack free time, standard cure rate (hardness), peel strength, application time and viscosity of the polymer base compound.

2.4 Changes in Cure Rate with Storage Time

Cure rates of the stored commercial sealants were monitored together with those of polymer base compounds cured with a reference curing agent and the commercial cure pastes against a standard liquid polymer. Plugs of sealant were formed using a small flat bottomed plastic cup as a mould and hardening of the sealant was progressively

assessed. The following mix ratios were employed (parts by weight given in parenthesis):

- (a) PR-1422 base compound (100), ammonium dichromate solution (10);
- (b) PR-1750 A Class base polymer (100), manganese dioxide paste (10);
- (c) PR-1750 B Class base compound (100), manganese dioxide paste (10);
- (d) LP-32 (100), PR-1422 A or B cure paste (10);
- (e) LP-32 (100), PR-1750 A or B cure paste (6).

These optimum mix ratios were determined through surveys in which the quantities of cure paste for each gram of liquid polymer were varied from 2.5 to 25 parts by weight (manganese dioxide cures) and 10 to 30 parts by weight (ammonium dichromate cures).

2.5 Chemical Analysis

2.5.1 Thiol Content of Polymers in Base Compound

A solution of polymer base compound in analytical grade chloroform (5% w/w) was centrifuged until all suspended fillers had been deposited. The clear supernatant solution was decanted, transferred to a fixed path length cell (2 mm) and analysed by the infrared procedure [17] using the SH absorption at 2588 cm^{-1} to determine thiol concentration by comparison with the combination absorption band at 2645 cm^{-1} as internal reference.

2.5.2 Chromium (VI) Content of PR-1422 Cure pastes [18]

The weighed cure paste (0.1 - 0.2 g) was dispersed in water (80 ml) and a solution of sulfuric acid (10% v/v) and phosphoric acid (7.5% v/v) (12 ml) was added. The mixture was titrated potentiometrically using ammonium ferrous sulfate (0.1 N) with platinum and saturated calomel electrodes. A digital multimeter was used to measure the electrode potential.

2.5.3 Manganese (IV) Content of PR 1750 Cure Pastes [8,14]

The weighed cure paste (0.1 - 0.2 g) was dispersed in analytical grade acetone and centrifuged. The solvent was decanted and the deposited solid dispersed in water. Solutions of potassium iodide (6 g) and disodium hydrogen phosphate (6 g) in water (20 ml) and phosphoric acid (25% v/v; 10 ml) were added. The mixture was stirred (1 h) and then titrated using sodium thiosulfate (0.1 N) and starch indicator.

2.6 Loss of Volatiles from Packaged Formulations

Evaporation of solvent from Semkits and the cure pastes of PR-1436 B 2 and PR 1750 B 2 stored at 25°C was determined by periodic measurement of weight losses. Simulated systems were produced by loading polyethylene sealant cartridges (Semco No. 6, 70 g) with mixtures of either calcium carbonate (Commercial Minerals

Superfine Whiting Omyacarb 10) and solvent (100 : 30 w/w) or LP-32 and solvent (90 : 10 w/w) and sealing each end with the appropriate caps and plugs.

Uniform dispersion of solvent into LP-32 was achieved using a mechanical blade mixer. A blend of LP-32, calcium carbonate and toluene (60 : 30 : 10 w/w) was also prepared by repeatedly passing the mixture through a triple roll mill. One set of the calcium carbonate-solvent series was enclosed in a heat sealed wrapping of polyester film coated with vapour deposited aluminium. All cartridges were stored at 25°C and weight losses were monitored with time.

3. RESULTS AND DISCUSSION

3.1 Packaging of Two-part Sealants

At the commencement of this study, aircraft sealants were supplied with the polymer base compound in a metal can. Manganese dioxide-based cure pastes were provided in sealed plastic containers while the dichromate-based cure systems, which contain volatile components, were packaged in both glass jars (PR-1422 series) and plastic tubs (PR-1436G). During the latter stages of the investigation, Air Office changed their procurement policy to allow acquisition of the Semkit style of sealant packaging. This system, depicted in Figure 1, is of plastic construction and allows the two components of the sealant to be mixed within the container, either by hand or with a motorised mixer. The Semkit containing the mixed sealant can then be used as a dispensing cartridge in conjunction with an application gun. The storage investigation embraced both types of sealant packaging.

3.2 Sealant Formulations

The study of commercial sealants indicated that the polymer base compounds of the PR-1422 A and B-class sealants were of a similar composition, which differed from those for PR-1750 polymer base compounds. Within each class of curing agent it was established that the same reagents were used with the differences resulting only from the varying proportions of the components (8).

The commercial dichromate curatives in this study were comprised of ammonium dichromate whereas for the more recent products used in the composition study, examination showed the cations to be calcium and/or magnesium (8). This difference would not be expected to influence the conclusions reached from the ageing investigations.

3.3 Effect of Temperature on Properties of Sealants Packaged in Cans

3.3.1 Materials and Procedure

The PR-1750 and PR-1436G sealants were manufactured in USA whereas the PR-1422 sealants were produced locally. The duration between date of manufacture and commencement of controlled storage is shown in Table 1. In all cases a significant proportion of the shelf life had elapsed prior to receipt of the materials and the thermal history of the sealants during this period was unknown. The initial examination of the ten sealants established that the following did not comply with

specification requirements : PR-1422 A-1/2, PR-1422 A-2 and PR-1750 B-6 (standard cure rate unsatisfactory), PR-1422 B-1/2 and PR-1750 A-2 (viscosity above limit) while the application life of PR-1750 A-2 also failed to meet the stipulated condition. With these sealants an indication of the temperature dependence of these properties was often possible through examination of the subsequent decline in performance with storage time. For PR-1422 B-2, however, it was impossible to obtain a satisfactory sealant mix after 13 months and further assessment was abandoned. The poor performance of this sealant was uncharacteristic since different batches of PR-1422 B-2 which had been used for other purposes have been stored under refrigeration ($\leq 2^{\circ}\text{C}$) without significant decline in properties for periods exceeding 2 years. A later batch of PR-1422 B-2 was acquired and performed satisfactorily in a survey limited to two years.

Evaluations were conducted at approximately 6 (initial), 12, 16, 24 and 36 months after the date of manufacture following storage at 25°C , 13°C , 2°C and -16°C . These temperatures correspond to conditions in a controlled environment laboratory, a temperature controlled storage room, a domestic refrigerator and a domestic freezer respectively. Absolute property values were recorded to allow trends to be discerned which may otherwise have been masked with sealants manufactured with little margin of tolerance with respect to particular specification requirements. Occasional inconsistencies between consecutive samplings of the same material have been attributed to packaging deficiencies (allowing ingress of air), difficulties in mixing highly viscous components and to experimental variation. Wherever such discrepancies were noted the overall trends were considered in the assignments of time to failure which are summarised in Table 2.

3.3.2 Viscosity of the Polymer Base Compound

The viscosity of the polymer base compound was the most temperature sensitive of the properties examined. Whereas changes in viscosity at -16°C over extended periods were insignificant and little different from the expected variations in measurements, at 25°C marked increases were generally observed (Table 3). These effects are exemplified by the 1750 B-class polymers. Storage of the lower viscosity A-class base polymers at 25°C produced less dramatic changes than with the B class materials. With the latter, viscosity increases were associated with gelation on the surface of the polymer base compound and with time a thick, hard skin formed. Skinning developed rapidly after the specification limit of 16000 poises was exceeded. Removal of the skin usually exposed materials of acceptable viscosity which also afforded sealants which cured satisfactorily. Results obtained by this means, however, are listed only for purposes of comparison. At $13-25^{\circ}\text{C}$ the specification levels for B-class sealants were generally exceeded after 10 months (with the notable exceptions of PR-1750 B-2 and PR-1436G B-2). Storage at 2°C and -16°C , however, permitted an extension of satisfactory service life to at least 24 months.

Available data support the inference that the viscosities of both PR-1750 and PR-1422 polymer base compounds change to a similar degree during storage. As earlier findings indicated that no appreciable interaction occurs between the polysulfide polymer and phenolic resin adhesion additive [8] in the polymer base compound, the increase in viscosity is attributed to oxidation by air and formation of heavy surface skins supports this conclusion. Oxidation leads to partial cure of the polysulfide polymer and a product of increased molecular weight. Relationships between molecular weight and viscosity have been developed for polysulfide liquid polymers but are not directly applicable to filled systems [1,10]. The increase in

molecular weight of the polymer in the base compound can also be inferred from the changes in the cure rate and thiol content as discussed below.

3.3.3 Cure Rate

The effect of temperature on performance was also apparent upon monitoring rates of cure. At 2°C and -16°C nearly all sealants met the specification requirement after 36 months whereas at higher temperatures shorter times to failure were observed. A notable difference between dichromate and manganese dioxide curing systems became evident at 25°C. With time the dichromate cure pastes dried out and in some cases all the liquid viscosity adjuster (water-dimethylformamide) had evaporated leaving a dry powder. Such instances are identified in Table 4. Mixing in these cases was difficult and the measurements conducted on the cured products are not considered to be particularly meaningful. No indication of such behaviour occurred with the manganese dioxide cure pastes. Separate storage studies were conducted on cure pastes of PR-1436 B-2 and PR-1750 B-2 which are packaged in plastic containers. After storage at 25°C the respective weight losses were 0.02% and 0.1% after 18 days, 0.4% and 0.2% after 9 months and 0.7% and 0.4% after 20 months.

There were no distinctive differences discernible between A and B-class sealants although with the A type materials the extent of the changes associated with cure rate were less marked than those found with viscosity. Polymer base compounds which had developed a skin could be cured satisfactorily if material beneath the crust was used. Although this is not recommended as normal maintenance practice, it was demonstrated that this technique could be adopted should no other sealant stocks be available.

The cure rate of the sealants became slower on ageing but, with extended cure times, products of satisfactory hardness could be obtained. This is explicable in terms of the gradual development of higher molecular weight polymers in the base compound (as evidenced by viscosity changes). The reactivity of the polymer base compound reduces with increasing molecular weight [2,4], due to decreased mobility and lower thiol content.

3.3.4 Tack Free Time and Application Life

These properties provide an indication of the handling and application characteristics of freshly mixed sealants rather than a guide to the performance of cured material. Both are dependent on rate of cure and in the case of application life, the viscosity of the base polymer base compound can be important. The above observation that cure rate slows with increasing storage life is therefore of relevance. Application life, which is assessed either by viscosity of the mix or through an extrusion procedure was assisted by the gradual retardation of cure and for storage temperatures of 2°C and below all sealants met the specification requirement after 36 months (Table 5). At the higher storage temperatures, mixing difficulties imposed by skinning were the limiting factor. Again, removal of the skin exposed material which then performed satisfactorily.

In the case of tack free time the slowing cure rate reduces the capability of the mixed sealant to meet the specified provisions. The benefits of low temperature storage relative to room temperature conditioning are clearly shown by reference to Table 2.

3.3.5 Peel Strength

The results in Table 6 indicate that peel strength is practically insensitive to storage temperature. Only at 25°C did some restrictions occur and these were due to skinning and drying of the cure paste which prevented satisfactory mixing. For all tests the failure mode was 100% cohesive which indicates that prolonged storage has no deleterious effect on the adhesion additive. Moreover, increases in the molecular weight of polymer base compound clearly do not affect the tear strength of the resulting cured sealants.

3.3.6 Storage Lifetimes of Sealants

Suggested sealant shelf lives at various storage temperatures, from an analysis of the above results, are presented in Table 7. No differentiation is made between sealant classes and grades other than the observation that dichromate cure pastes are prone to dry at 25°C and therefore useful life is restricted to the lower limit of the suggested ranges. This proviso does not apply to manganese dioxide-cured systems.

The guide in Table 7 includes elapsed time before receipt of the sealants during which it is assumed that they were exposed to mild transit temperatures. Extensions of storage life beyond those indicated could reasonably be expected with shorter delivery times. Allowances were made for those sealants which performed only moderately on receipt and the absolute performance trends on storage were used in these cases. The probability of aberrations due to batch variation is also recognised.

While the advantages of low temperature storage are readily evident, the additional benefits which result from freezer storage (-16°C) relative to those provided by a domestic refrigerator (2°C) are debatable. Marginally better performance properties were recorded at the lower temperature but these were not reflected in the assessed storage lives (Table 7). In this context it is relevant that a series of PR-1422 sealants (A-1/2, A-2, B-1/2 and B-2) which were separately maintained at -40°C were still in acceptable condition after 5 years. Therefore it is suggested that use of freezers in a central storage depot would provide optimum storage and allow benefits such as planned procurement and reduced wastage to be maximised.

3.4 Changes in Activity of Sealant Components

Attempts were made to relate the above property changes to measurable trends in the activities of the polymer base compounds and curing agents. This was pursued by measuring thiol concentrations of the polymer in the base compounds, chromium (VI) or manganese (IV) concentrations of the cure pastes and periodically during storage following the curing rates of

- (a) the polymer base compounds against a standard curing agent and
- (b) the PR-1750 and PR-1422 cure pastes against a standard liquid polymer.

Spectroscopic techniques were also used in an endeavour to identify chemical changes in the polysulfides.

3.4.1 Thiol Contents of Polymer Base Compounds

Temperature dependence of the thiol concentration of the polymer base compounds is shown as a function of storage time in Table 8. Analyses were carried out by the infrared procedure of Davidson and Mathys [17] which was developed in order to avoid problems associated with titrimetric techniques [8]. Care was necessary during manipulations prior to the spectroscopic measurements. Removal of fillers involved centrifugation of a chloroform solution containing the dispersed polymer base compounds. In the cases of the longer aged PR-1750 polymer base compounds the thiol concentration was found to be a function of centrifuging time. Shorter periods resulted in cloudy solutions with appreciably higher thiol contents than unaged polymers. This effect was partly attributed to baseline distortion caused by residual calcium carbonate particles. Longer centrifugation periods gave layered solutions with the top clear layer of lower molecular weight and thiol content than the lower turbid phase which had a gel-like consistency. It is considered that with extended centrifuging times differential packing of the polymer could occur with the higher molecular weight (and less soluble species) eventually separating from the solution. The times which produced the best compromise between these effects were established (generally 15-20 min) and adherence to these within each class of PR-1750 sealant permitted good reproducibility. These problems were not encountered with PR-1422 sealants. All measured thiol contents were in the range of linear correlation for the spectroscopic technique and in all assessments over the storage period measurements of the thiol concentration of LP-32 polymer samples taken from a bulk container were included as a reference. Subsequent to obtaining the measurements listed in Table 8 it was ascertained that toluene and methyl ethyl ketone, both components of A class polymer base compounds, exhibit small overtones in the 2585 to 2590 cm^{-1} region. The figures for the A class materials are therefore not absolute (values of 1.2% for PR-1422 and 2.15% for PR-1750 prepolymers are typical). The lower results which were noted at 13°C and 25°C for some sealants are, however, not considered to reflect solvent loss since viscosity is unaltered. The measurements for any given sealant are therefore internally consistent.

3.4.2 Mn(IV) and Cr(VI) Content in Cure Pastes

The changes in concentration of Mn(IV) in PR-1750 and Cr(VI) in PR-1422 cure pastes were monitored during the study and results are summarised in Tables 9 and 10 respectively. The Mn(IV) content was determined using a procedure, described previously [8], which was a modification of that outlined by Riedel de Haën [14]. The use of acetone overcame difficulties arising from the attempted dispersal of the cure paste in an aqueous medium. A standard potentiometric titration procedure [18] was used to determine Cr(VI).

3.4.3 Cure Rate Studies

Changes in activity of the cure pastes of PR-1750 and PR-1422 were assessed by regular measurement of the degree of cure of mixtures with a standard polysulfide polymer, LP-32 (Tables 11,12). For each curing system preliminary studies were carried out to establish optimum mix ratios using ranges of 4 to 40 parts of curing agent to 100 parts of LP-32. Changes in activity of the stored polymer base compounds were also followed similarly using an ammonium dichromate-dimethylformamide-water curing mixture for PR-1422 polymer base compounds (Table 13) and a paste of manganese dioxide in di-(2-ethylhexyl) phthalate for the PR-1750 series (Table 14). Two grades of Riedel de Haën manganese dioxide, FA and C, were examined for this purpose but for curing within practical time limits only the type C

reagent was suitable. In all cases the minimum quantity of cure paste necessary to effect a satisfactory cure with fresh polymer base compound was selected to accentuate any activity changes : with excess of cure paste little differentiation between aged samples was possible.

3.4.4 Other Analytical Techniques

The ageing base polymer compounds were also examined using GPC and ^1H nmr but neither procedure was diagnostic and any changes which were noted were too insignificant to be meaningful.

3.5 Analysis of Storage Performance of Canned Sealants

No substantial differences were noted between sealants of different classes (A or B) within the same sealant type. The most significant storage effect was the temperature dependence of the viscosity of the polymer base compound. Substantial increases in viscosity were noted at storage temperatures of 25°C and in most cases this was associated with the development of a skin on the surface. It was concluded that this resulted from oxidation by air leading to material of higher molecular weight and eventual polymerisation at the surface. Removal of the skin provided access to acceptable underlying material which generally could be cured without difficulty.

This process should be associated with a drop in thiol concentration. Although such trends were discernible the extent was somewhat masked by the limitations of measurement since the oxidation was a surface effect and removal of the skin merely exposed material which was virtually unchanged. Any drop in thiol concentration leads to a slowing of the cure rate but the ultimate hardnesses of the sealants obtained under such conditions were of the same order as those from components which complied with specification requirements. It should be noted that as cure rate slows the application life (which is monitored by extrusion rate or viscosity) this requirement is more readily achieved and as a consequence such measurements are not particularly informative. The peel strength of the sealants appeared to be unaffected by storage and as this would be dependent primarily on the condition of the adhesion additive these results further support the finding that the phenolic resins are unreactive in the absence of an acid catalyst [8].

The other significant effect which is also manifested after storage at 25°C is loss of solvent from the dichromate cure pastes stored in polythene containers. This did not appear to be a problem with the manganese dioxide curing agents which do not have volatile components other than small quantities of water. The solvent loss is gradual and leads first to a thickening of the dichromate cure paste but eventually a powder is formed. While it would be possible to reconstitute dried pastes it is not a practical consideration for maintenance operations. Moreover, the reactivity of metals with dichromate salts precludes the use of cans to prevent solvent loss.

Although changes in Mn(IV) and Cr(VI) concentrations with time were monitored at various temperatures, the observed changes were slight. The results obtained for Cr(VI) were, in part, affected by the solvent loss described above. As a considerable excess of curing agent is used in the sealant systems (about threefold), any minor decline in metal ion concentration is insignificant in practical terms. The most important considerations are therefore the retention of activity of the

manganese dioxide system (since an activated grade is necessary for sealant cure), the ease of mixing of dried dichromate pastes and the ability of the dried paste to cure the polysulfide in the absence of water which is considered to be essential for the curing reaction to proceed [13]. These effects were assessed by preparation of LP-32 liquid polymer based sealants using stored cure pastes. Some indication of the problems which arise from drying of the dichromate pastes is evident from the results shown in Table 12 where the sealant from the PR-1422 A-2 system stored at 25°C and 16°C (which was in a powdery state) exhibited a poor degree of cure; the incompletely dried pastes of the A-1/2 and B-1/2 systems still performed satisfactorily. With the manganese dioxide cure pastes (Table 11), storage at 25°C caused a perceptible decline in hardness of LP-32 liquid polymer based sealants, particularly after 25 months storage. As this is not related to the Mn(IV) concentration the effect is ascribed to a decline in activity of the manganese dioxide. Neither type of curing system showed any loss of performance when stored at, or below, 2°C.

The use of reference cure pastes to monitor changes in reactivity of the polymer base compound with storage was not particularly informative. The reference dichromate curing systems were most effective but results were obtained only to 16 months storage and no trends were detected over this period (Table 13). The reference manganese dioxide cure paste did not contain the accelerators incorporated in commercial curing agents [8]. The cure rates achieved were consequently not comparable to those with the components of the stored commercial materials but it was expected that the relative degree of cure could have been indicative of activity changes in the base polymers (Table 14). A further complication involved the use of mobile polymer base compound from beneath the skin of oxidised polysulfide - acceptable cures could be obtained in this manner from apparently defective material. Nevertheless, after significant storage times (25 months), and despite some erratic results, a trend to lower hardnesses of sealants from several polymer base compounds stored at 25°C could be discerned.

These observations were reinforced by the eventual hardnesses reached on curing the stored sealants for extended periods (Table 15). While acceptable products were obtained in almost all cases, those from 25°C storage for 25 months did exhibit a small but consistent decline in hardness relative to materials stored at lower temperatures. These results also indicate that any decrease in thiol concentration will not necessarily impair the properties of the fully cured sealant, although cure rate may be somewhat retarded.

It is therefore confidently predicted that maintenance of sealant components at low temperatures will considerably increase storage life in accord with the expectations listed in Table 7. The sealants used in this study were acquired after a considerable period of their approved storage life had elapsed. Acquisition of sealants soon after manufacture could be expected to result in further extension of storage life at the indicated temperatures. While some changes in sealant composition may occur between different batches it appears that the additives have little influence on storage stability. For this reason it is unlikely that products obtained from various overseas sources would differ greatly in storage performance. The only factor worth consideration in this context would be the quality of the calcium carbonate filler since the basicity of the polymer component will influence the rate of oxidation in air [13].

3.6 Sealants in Semkit Form

A range of PR-1422 and PR-1750 Semkit formulations (Figure 1) were acquired and details are given in Table 16. All were sourced in Australia except for PR-1750 B-6 which was obtained from PRC in California. Storage performance is also listed in Table 16. These results were significantly influenced by two factors. Firstly, local production of Semkits had only recently commenced and many batches were unacceptable on receipt or only marginally met specification requirements. The second important feature was the use of cardboard for packaging the Semkit containers. This differed from the overseas method, exemplified with PR-1750 B-6, which entailed enclosing the sealant capsule in a laminated sheath of aluminised polyethylene.

In addition, locally produced Semkits developed noticeable air gaps both above the upper surface of compounded polymer and at the plunger while a solvent vapour was evident on opening the cardboard containers. Transmission of solvent through the high density polyethylene walls of the Semkit was shown to occur readily. At 25°C the PR-1422 A-2 sealant exhibited weight losses of 0.07%, 0.14%, 0.28%, 0.46% and 1.17% after 3, 6, 10, 16 and 20 months respectively while PR-1422 B-2 which contains little volatile material gave a loss of 0.04% after 6 months. Studies with polyethylene sealant cartridges containing various mixes of solvent and calcium carbonate filler substantiated these findings (Table 17). Surrounding these cartridges with aluminised polyethylene seals reduced solvent loss by around 50%.

In the absence of the outer seal the Semkits not only lose solvent but air can also enter the container. Oxidation of the polymer base compound leads to curing within the Semkit and this reaction is assisted by alkaline conditions. Due to compounding, the PR-1750 polymer base compounds are more basic than those of the PR-1422 series [8] and this was manifested through a rapid increase in viscosity soon after storage coupled with pronounced skinning at each end of the PR-1750 Semkits. In many instances this caused breakage of the mixing rod when attempts were made to activate the sealant cure. Under these conditions hand mixing was not possible. Similar effects were noted in the PR-1422 Semkits but these occurred at a slower rate.

The PR-1750 B-6 samples which were packaged in a protective sheath performed quite well under storage and at temperatures of -16°C and below afforded storage lives of at least 18 months. The marked improvement in performance of this sealant relative to locally made materials is attributed in the main to the use of the aluminised polyethylene wrapping which retards oxidation of the polymer base compound.

These results are similar to, but, not entirely consistent with, those of the only other reported study of this type in which Chemseal CS 3204 A-1/2, B-1/2 and B-2 sealants (manganese dioxide cured, meet MIL-S-8802), packaged in plastic injection kits, were stored for 12 months under fluctuating temperature conditions [19]. Exposure was carried out using various states of external packaging: Mylar-lined aluminium foil bags, clear polyethylene bags and no protection. Skinning of the polymer base compound was noted in all cases but was more prevalent in the B-class materials. While the A-1/2 sealant performed better when sealed by the Mylar-lined aluminium foil bag, the B-class sealants were unaffected by external packages. From the present investigation it is clear that the presence of an external seal has a critical effect on the storage life of B-class sealants. The divergence in performance observed in the studies may reflect the differences in permeability of the external

sheaths. Although only the PR-1750 B-6 sealants were available for assessment, the beneficial effect of an external, impermeable seal coupled with low temperature storage is dramatically highlighted.

It would be expected that for any given sealant its storage lifetime when packaged in cans would exceed that in the Semkit form. The aluminised plastic seal which is used to protect the Semkits is not completely impermeable (Table 17) since vacuum deposited metal films can contain minor flaws and pinholes. Therefore, provided the lids are properly secured, cans will offer better resistance to both ingress of air and loss of solvent. The results with the PR-1750 B-6 Semkit support this conclusion.

4. CONCLUSIONS

The following features of the effect of temperature on the storage of polysulfide aircraft sealants have been established.

- (a) At temperatures of 25°C the manufacturer's stipulated storage life of 9 months is a reasonable guide. Considerable extension of storage life can be achieved at lower temperatures and at 2°C and below sealants packaged in cans can be maintained for two to three years and still meet all specification requirements. For storage at low temperatures little difference was noted between the performances of A and B class sealants and the type of curative used had virtually no influence.
- (b) Sealants packaged as Semkits could also be stored for longer periods at temperatures of 2°C and below but with this packaging system the need to protect the polymer base compound from oxidation was of greater importance. Use of a laminated sheath of aluminised polyethylene allowed storage to be extended to at least 18 months. Canned sealants, however, are able to be satisfactorily stored for significantly longer periods than are Semkits.
- (c) Most sealants in the study were acquired several months after manufacture. It is to be expected that sealants placed in low temperature storage immediately after manufacture could be stored for somewhat longer than the 2 to 3 years observed in this investigation.
- (d) The causes of failure were shown to be oxidation of the polymer base compound (which leads to skinning, increased viscosity and a drop in thiol content) and loss of solvent from the dichromate-based cure pastes.
- (e) Concentrations of Mn(IV) and Cr(VI) in the curatives did not change on storage and peel strength was also unaffected.
- (f) Introduction of low temperature storage of sealants by RAAF should reduce wastage and simplify procurement. At current usage rates, storage in freezers would be expected to provide cost savings of the order of \$500,000 per annum.

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Table 1 Polysulfide Sealants and Storage History

Sealant		Date of Manufacture	Date Storage Commenced
Type	Class		
PR-1750	B-1/2	October 80	March 81
PR-1750	B-2	October 80	March 81
PR-1750	B-6	October 80	March 81
PR-1750	A-1/2	October 80	March 81
PR-1750	A-2	November 80	May 81
PR-1422	A-1/2	July 80	March 81
PR-1422	A-2	August 80	March 81
PR-1422	B-1/2	August 80	June 81
PR-1422	B-2	September 80	March 81
PR-1422	B-2	May 85	May 85
PR-1436G	B-2	September 80	March 81

Table 2 Time to Failure (Months) of Sealants stored at Various Temperatures *

Sealant	Temp (°C)	Viscosity	Tack Free Time	Cure Rate	Peel Strength	Application Life
PR-1422 A-1/2	25	12	16	12 [†] , [¶]	16	24
	13	24	>36	24 [†]	>36	>36
	2	24	>36	36 [†]	>36	>36
	-16	36	>36	>36 [†]	>36	>36
PR-1422 A-2	25	>36	6	12 [†] , [¶]	16	24
	13	>36	24	12 [†]	>36	>36
	2	>36	24	24 [†]	>36	>36
	-16	>36	24	>36 [†]	>36	>36
PR-1422 B-1/2	25	<6 [†]	24	24 [¶]	12	24
	13	<6 [†]	24	24	>36	24
	2	<6 [†]	>36	>36	>36	24
	-16	<6 [†]	>36	>36	>36	24
PR-1422 B-2 [#]	25	10 ^{††}	12	12 [¶]	12	16
	13	10 ^{††}	12	12	12	16
	2	12 ^{††}	12	12	12	16
	-16	12 ^{††}	12	12	12	16
PR-1422 B-2 ^{¶¶}	25	16	24	24	>24	16
	13	24	24	24	>24	24
	2	>24	>24	>24	>24	24
	-16	>24	>24	>24	>24	24
PR-1750 A-1/2	25	>36	24	16	>36	>36
	13	>36	>36	24	>36	>36
	2	>36	>36	36	>36	>36
	-16	>36	>36	36	>36	>36

Table 2 (continued)

Sealant		Temp (°C)	Viscosity	Tack Free Time	Cure Rate	Peel Strength	application Life
PR-1750	A-2	25	20 [†]	>36	12	>36	>36
		13	20 [†]	>36	>36	>36	>36
		2	36 [†]	>36	>36	>36	>36
		-16	36 [†]	>36	>36	>36	>36
PR-1750	B-1-2	25	12	24	9	24	24
		13	24	24	24	>36	24
		2	24	>36	>36	>36	>36
		-16	24	>36	>36	>36	>36
PR 1750	B 2	25	24	24	12 ^{**}	>36	>36
		13	24	24	16 ^{**}	>36	>36
		2	24	24	>36 ^{**}	>36	>36
		16	24	24	>36	>36	>36
PR 1750	B 6	25	9	12	9 [*]	>36	>36
		13	12	24	12 [†]	>36	>36
		2	24	24	24 [†]	>36	>36
		16	24	24	24 [†]	>36	>36
PR 1336G	B 2	25	24	12	24 [†]	24	>36
		13	24	>36	24	>36	>36
		2	24	>36	>36	>36	>36
		16	24	>36	>36	>36	>36

- * Tested to requirements of MIL S 8802 or MIL S 83430 as appropriate.
- † Initial measurement was below specification, times before which a noticeable decline occurs are given.
- ‡ Cure paste of 25°C sample showed evidence of drying out at 20 to 24 months.
- ... Viscosity became too high to allow mixing after 12 months.
- # Initial reading just met requirement; only a slight decline occurred subsequently.
- ## First series.
- ** Second series.

Table 3. Variations in Viscosity of Polymer Composites with Storage

Polysulfide Base Polymer* (Initial viscosity poises, sampling time, months)	Viscosity (poises)																		
	20						25						36						
	25	33	36	25	33	36	25	33	25	33	25	33	2	-16					
PR-1422 A-1/2 (350, 6 m)	450	390	350	520	480	460	420	530	450	420	380	530	450	450	380	790	680	620	500
PR-1422 A-2 (190, 5 m)	230	220	210	200	260	245	230	220	270	250	240	330	270	250	200	450	350	330	250
PR-1422 B-1/2 (11200, 7 m)	217900	16900	17700	16000	>200000	>200000	>200000	19600	all >20000	18000	18000	18000	18000	18000	17500	all >20000			
PR-1422 B-2† (13200, 7 m)	17000	17000	15000	15000	17800	17000	16000	16000	all >20000										
PR-1750 A-1/2 (400, 5 m)	440	420	420	400	410	400	420	400	440	430	450	440	430	450	410	480	480	480	410
PR-1750 A-2 (650, 6 m)	480	530	630	590	780	630	630	740	780	630	630	780	630	630	740	950	720	680	670
PR-1750 B-1/2 (15400, 5 m)	11800	14000	12800	17000	>20000	19800	16000	15000	13400	15000	14800	14500	14800	14500	14500	† >20000	>20000	>20000	>20000

Table 3 (continued)

Polysulfide Base Polymer* (Initial viscosity poises, sampling time, months)	Viscosity (poises)														
	Storage Time (months)						Storage Temperature (°C)								
	12	13	2	-16	25	13	2	-16	25	13	2	-16			
PR-1750 B-2 (12000, 5 m)	13500	12000	12000	13600	14000	12600	14000	13400	16000†	14400	14000	14000	all >20000†		
PR-1750 B-6 (12780, 5 M)	16900	16000	14600	14900	>20000†	18400	15000	15800	14400†	13400†	13000	13200	18000†	18000†	17000
PR-1436G B-2 (14300, 6 m)	4800	14000	13900	13800	14600	12400	14400	12500	15600	15600	15400	13000	all >20000		

* Specification requirements: A-cl. polymers, 100-500 p; B-class polymers, 6000-16000 p

† Skin developed, measurement on material underlying the skin

‡ First series

Table 4 Variations in cure rate with storage

Polysulfide Sealant (Initial Hardness Reading, sampling time, months)*	Hardness after Specified Curing Period															
	Storage Time (months)						Storage Temperature (°C)									
	12	16	20	25	36		12	16	20	25	36					
PR-1422 A-1/2 (30, 6 m)	25	13	2	-16	25	13	2	-16	25	13	2	-16	25	13	2	-16
PR-1422 A-2 (27, 5 m)	36	34	35	37	29†	29	30	30	23†	25	27	28	25†, 28†	29†	29†	32†
PR-1422 B-1/2 (48, 7 m)	27	25	30	28	19	16	28	28	15†	20	25	29	15†	18	21	30
PR-1422 B-2* (42, 6 m)	45	45	47	49	†	†	†	†	40†	38	40	43	40†, ††	41	40	40
PR-1750 A-1/2 (35, 5 m)	34	36	37	35	33	35	34	34	24	33	37	34	24	31	32	33
PR-1750 A-2 (38, 6 m)	34	32	38	35	29	32	37	36	23	32	38	33	27	34	36	35
PR-1750 B-1/2 (35, 5 m)	32	33	34	35	32††	33	34	35	32††	34††	32	35	-	34††	37	35

Table 4 (continued)

Polyulfide Sealant (Initial Hardness Reading Sampling time, months)	Hardness after Specified Curing Period																							
	12				16				20				25				36							
	Storage Time (months)	Storage Temperature (°C)	Hardness	Reading	Storage Time (months)	Storage Temperature (°C)	Hardness	Reading	Storage Time (months)	Storage Temperature (°C)	Hardness	Reading	Storage Time (months)	Storage Temperature (°C)	Hardness	Reading	Storage Time (months)	Storage Temperature (°C)	Hardness	Reading				
PR-1750 B-2 (35, 5 m)	25	13	2	-16	25	13	2	-16	25	13	2	-16	25	13	2	-16	25	13	2	-16				
	27	26	26	28	21	31	35	32	†	†	†	†	24	28	29	30	24	††	27	††	32			
PR-1750 B-6 (30, 5 m)	24	30	32	34	15	20	34	30	20	††	††	31	††	31	31	35	8	††	12	††	22	††	25	
	43	50	49	48	36	44	40	43	45	†	46	47	45	24	†	31	35	39						
PR-1436G B-2 (50, 6 m)																								

* Specification requirements: PR-1422 A-1/2, 35 at 40 h; PR1750 A-1/2 and B-1/2, 35 at 30 h; PR-1750 B-2 and PR-1422 A-2, B-2, 35 at 72 h; PR-1436 B-2 and PR-1750 A-2, 35 at 48 h and PR-1750 B-6, 30 at 120 h.

† Cure paste dried out

†† Skin on polymer base, underlying material used for evaluation

** First series

† Hardnesses of 36 to 40 obtained after 96 h cure time

Table 5 Variations in application life with storage

Polysulfide Sealant (Initial measurement)*	Application Life													
	Storage Time (months)						Storage Temperature (°C)							
	12	13	16	25	13	2	20	25	13	2	25	13	2	36
PR-1422 A-1/2 (1000 P, 6 m)	1120	880	880	880	880	880	880	880	880	880	880	880	880	880
PR-1422 A-2 (368 P, 5 m)	640	680	680	680	680	680	680	680	680	680	680	680	680	680
PR-1422 B-1/2 (20 g/m, 7 m)	13	13	16	16	16	16	16	16	16	16	16	16	16	16
PR-1422 B-2** (33 g/m, 6 m)	45	48	51	50	50	50	50	50	50	50	50	50	50	50
PR-1750 A-1/2 (900 P, 5 m)	1000	1000	800	880	880	880	880	880	880	880	880	880	880	880
PR-1750 A-2 (2800 P, 6 m)	3000	2940	1780	1600	1600	1600	1600	1600	1600	1600	1600	1600	1600	1600

Table 5 (continued)

Polysulfide Sealant (Initial measurement)*	Application Life*											
	Storage Time (months)						Storage Temperature (°C)					
	12	13	2	-16	25	13	16	13	2	-16	25	13
	25	42	40	44	44	44†	46	45	45	45	45	45
PR-1750 B-1/2 (44 g/m, 5 m)												
PR-1750 B-2 (25 g/m, 5 m)	31	33	30	44	32	33	33	33	35	35	35	35
PR-1750 B-6 (26 g/m, 5 m)	35	44	32	35	35	42	38	35	35	38	35	35
PR-1436G B-2 (35 g/m, 6 m)	84	130	95	110	95	110	180	110	110	110	110	110

* Specification requirements: A-classes, 2500 poises; B-classes, 15 g/m at end of rated application time
 † Cure paste dried out;
 ‡ Mix unable to be obtained;
 †† Skin, underlying material used for evaluation;
 ** First series

‡ Sealants met requirement, no absolute figures

Table 6 Changes in Peel Strength with Storage

Polysulfide Sealant (Initial peel strength measurement)*	Peel Strength (N/2.5 cm)																			
	12				16				20				25				36			
	25	13	2	-16	25	13	2	-16	25	13	2	-16	25	13	2	-16	25	13	2	-16
Storage Temperature (°C)																				
PR-1422 A-1/2 (102, 6 m)	76	102	98	91	85	80	93	125	58	80	98	116	62	76	80	80	-	98	98	107
PR-1422 A-2 (98, 5 m)	111	91	133	138	85	98	85	91	62	89	147	98	62	89	147	98	-	102	111	125
PR-1422 B-1/2 (111, 7 m)	89	102	91	151	67	89	89	107	76	¶	¶	¶	80 [†]	89	98	98	-	111	98	120
PR-1422 B-2 ^{††} (125, 6 m)	107	133	129	129																
PR-1750 A-1/2 (>178, 5 m)	129	129	89	98	89	89	120	156	89 [¶]	89 [¶]	111	113	89	120	102	120	93	111	111	102
PR-1750 A-2 (111, 6 m)	107	116	111	107	89	98	116	116	102	107	111	111	98	98	98	98	89	138	120	98

Table 6 (continued)

Polysulfide Sealant (Initial peel strength measurement)*	Peel Strength (N/2.5 cm)																			
	12				16				20				25				36			
	25	13	2	-16	25	13	2	-16	25	13	2	-16	25	13	2	-16	25	13	2	-16
Storage Temperature (°C)																				
PR-1750 B-1/2 (>200, 5 m)	129	129	129	107	147	147	160	160	160	160	160	160	169†	160†	142	178	-	178†	191	200
PR-1750 B-2 (89, 5 m)	107	71	102	107	130	129	†	†	†	93	138	156	156	98	107	120	125	80	125	†
PR-1750 B-6 (165, 5 m)	107	120	129	120	125	125	116	116					120	129	133	133	129	142	156	142
PR-1436G B-2 (93, 6 m)	80	93	80	98	71	71	89	76					71	80	80	85	-	71	71	71

* Specification requirements: PR-1422 and PR-1750 sealants, 89N/2.5 cm (20 lb/in width); PR-1436G, 67N/2.5 cm (15 lb/in width)

† Cure paste substantially dried out

‡ Faulty panel preparation

†† First series

Table 7 Temperature dependence of storage lives of polysulfide sealants

TEMPERATURE (°C)	STORAGE LIFE
-16	2 to 3 years
2	2 to 3 years
13	18 to 24 months
25	9 to 12 months

Table 8 Change in mercaptan content of polymers in base compounds with storage

Polysulfide Base Polymer	Storage Time (months)	% SH*			
		25	Storage Temperature (°C)		
			13	2	-16
PR-1422 B-1/2	12	1.12	1.15	1.15	1.16
	16	1.11	1.07	1.11	1.11
	25	1.11 [†]	1.14 [†]	1.17	1.21
PR-1422 B-2 [‡]	12	1.42	1.44	1.42	1.42
	16	1.38	1.38	1.41	1.41
PR-1422 A-1/2	12	1.34	1.41	1.41	1.43
	16	1.28 [†]	1.36	1.43	1.45
	25	1.25 [†]	1.32	1.37	1.43
PR-1750 A-1/2	12	2.51	2.38	2.44	2.45
	16	2.48	2.47	2.46	2.50
	20	2.51	2.45	2.45	2.45
PR-1750 A-2	12	2.02	1.98	2.13	2.22
	16	2.05	1.98	2.08	2.22
	25	2.04	2.00	2.08	2.27
PR-1750 B-1/2	10	2.06	2.05	2.18	2.21
	25	2.01 [†]	2.02	2.08	2.25
PR-1750 B-2	10	1.86	1.36	1.95	1.90
	12	1.87	1.85	1.88	1.82
	25	1.84	1.81	1.96	2.02
PR-1750 B-6	10	2.15	2.20	2.26	2.23
	16	2.00 [†]	2.05	2.15	2.18

* I.P-32 reference : [SH] varied from 1.52 to 1.62 over assessments.

[†] Skin formed on surface.

[‡] First series.

Table 9 Changes in manganese (IV) content of PR-1750 cure pastes with storage

Cure Paste	Storage Time (months)	% MnO ₂			
		Storage Temperature (°C)			
		25	13	2	-13
PR-1750 A-1/2	10	43.7	43.8	42.7	43.4
	16	43.6	44.4	44.4	44.4
	25	43.1	44.4	45.0	44.6
PR-1750 A-2	10	44.8	45.2	45.2	44.5
	13	44.7	45.6	45.1	44.9
	25	43.6	45.0	44.8	44.8
PR-1750 B-1/2	12	44.4	44.2	44.3	44.3
	25	42.7	43.5	43.9	43.9
PR-1750 B-2	10	46.9	47.8	47.0	46.8
	12	47.2	46.9	46.7	46.7
	25	46.3	46.7	46.6	46.7
PR-1750 B-6	12	41.1	42.3	42.7	42.7
	25	41.7	42.4	43.0	43.5

Table 10 Changes in chromium (VI) content of PR-1422 cure pastes during storage

Cure Paste	Storage Time (months)	% (NH ₄) ₂ Cr ₂ O ₇			
		Storage Temperature (°C)			
		25	13	2	-13
PR-1422 A-1/2	12	38.3	39.8	39.5	39.5
	16	36.8*	38.7	48.6	38.8
	25	37.5*	39.1	39.8	39.3
PR-1422 A-2	12	28.6	29.2	29.6	29.6
	16	25.6*	28.2	28.2	28.6
PR-1422 B-1/2	12	41.8	41.0	42.6	41.9
	25	37.4*	40.3	40.8	40.7
PR-1422 B-2 [†]	12	23.8	24.1	24.3	23.6
	16	23.9*	23.9	24.2	24.2

* Cure paste dried out

[†] First series

Table 11 Assessment of change in activity of PR-1750 cure pastes on storage : hardness of sealants derived from LP-32*

Cure Paste	Storage Time (months)	Hardness [†]			
		Storage Temperature (°C)			
		25	13	2	-16
PR-1750 A-1/2	12	34	34.5	36.5	36.5
	16	34	34.5	37	35.3
	25	32	35.6	35.3	35.3
PR-1750 A-2	12	24.8	27.2	24.6	23.6
	16	21.5	23.7	24.1	23.0
	25	20	25.8	24.1	24.2
PR-1750 B-1/2	12	36.3	36.6	38.7	37.4
	25	28.6	37.3	37.3	37.3
PR-1750 B-2	12	26.2	29.3	27.2	28.1
	16	25.8	27.7	28.6	28.7
	25	21.7	27.6	26.5	31.6
PR-1750 B-6	12	21.0	22.0	23.1	20.9
	16	18.1	22.1	21.4	23.5

* Sealants produced from 6 parts by weight of cure paste and 100 parts by weight of LP-32.

† A-1/2 and B-1/2 based sealants measured at 40 h, remainder at 24 h.

Table 12 Assessment of change in activity of PR-1422 cure pastes on storage : hardness of sealants derived from LP-32*

Cure Paste	Storage Time (months)	Hardness [†]			
		Storage Temperature (°C)			
		25	13	2	-16
PR-1422 A-1/2	12	47.4	45.7	47.1	45.2
	16	48.3 [‡]	47.8	46.7	46.3
	25	48.4 [‡]	45.9	45.1	46.3
PR-1422 A-2	12	38.2	43.6	45.3	45.9
	16	22.5 [‡]	41.8	44.1	42.9
	25	24.0 [‡]	40	36.1	40.9
PR-1422 B-1/2	12	43.5	43.5	43.6	44.3
	25	44 [‡]	42.8	43	42.1
PR-1422 B-2 ^{††}	12	18.7	28.4	31.5	25.7
	16	26	32.5	28.8	26.9

* Sealants produced from 10 parts by weight of cure paste and 100 parts by weight of LP-32.

[†] Measured at rated time for each class of sealant.

[‡] Solvent lost from cure paste.

^{††} First series.

Table 13 Assessment of change in activity of PR-1422 polymer base compounds on storage : hardness of sealants with a reference cure paste*

PR-1422 Base Polymer	Storage Time (months)	Hardness [†]			
		Storage Temperature (°C)			
		25	13	2	-16
PR-1422 A-1/2	12	27.3	27.8	28.9	28.9
	16	27.5	27.2	27.5	30.0
PR-1422 A-2	12	27.1	26.1	27.1	27.4
	16	25.1	26.3	27.0	27.0
PR-1422 B-1/2	12	45.3	44.2	44.6	45.8
	16	44.2	44.3	43.8	43.9
PR-1422 B-2 [‡]	12	38.8	38.9	38.9	37.6
	16	40.4	37.9	38.8	37.1

* Sealants produced from 100 parts by weight of the polymer base compound and 10 parts by weight of ammonium dichromate cure paste.

[†] Measured after 72 h.

[‡] First series.

Table 14 Assessment of change in activity of PR-1750 polymer base compounds on storage : hardness of sealants with a reference cure paste*

PR-1750 Base Polymer	Storage Time (months)	Hardness [†]			
		Storage Temperature (°C)			
		25	13	2	-16
PR-1750 A-1/2	12	25	15	21	18
	16	5	22	20	22
	25	27	20	26	24
PR-1750 A-2	12	23	28	43	45
	16	23	26	24	48
	25	30	24	40	38
PR-1750 B-1/2	12	33	25	39	31
	25	14	31	37	43
PR-1750 B-2	12	17	22	21	23
	16	13	19	8	17
	25	28	18	23	20
PR-1750 B-6	12	22	27	33	29
	16	34	32	30	27

* Sealants produced from 100 parts by weight of base polymer compound and 10 parts by weight of the reference manganese dioxide paste.

† Hardness measured after 192 h for A-1/2, A-2 and B-1/2 based sealants, others after 133 h.

Table 15 Change in activity of both polymer base compounds and cure pastes on storage : ultimate hardness of sealants

Poly-sulfide Sealant	Storage Time (months)	Ultimate Hardness			
		Storage Temperature (°C)			
		25	13	2	-16
PR-1422 A-1/2*	12	39	40	41	40
	16	40	42	42	41
	25	36	36	41	40
PR-1422 A-2†	12	27	30	30	31
	16	26	26	28	30
	25	26	26	29	31
PR1422 B-1/2†	12	57	58	57	55
	16	56	57	58	55
PR-1422 B-2†,†	12	45	45	44	45
	16	44	47	44	44
PR-1750 A-1/2†	12	41	42	42	43
	16	36	40	39	39
	25	38	40	42	40
PR-1750 A-2††	12	35	40	35	36
	16	34	33	39	35
	25	26	35	39	34
PR-1750 B-1/2**	12	34	37	36	34
	25	34	33	36	36
PR-1750 B-2#	12	40	41	40	41
	25	39	41	41	41
PR-1750 B-6††	12	29	33	34	34
	25	26	32	32	33

* measured after 96 h; † measured after 70 h; † first series;
 †† measured after 60 h; ** measured after 48 h; # measured after 120 h;
 †† measured after 144 h.

Table 16 Polysulfide Semkits and storage performance

Semkit	Date of Manufacture	Date of Receipt	Storage Lifetime(months)			
			-16°C	2°C	13°C	25°C
PR-1422 A-1/2	October 84	October 84	12	12	7	7
PR-1422 A-2	July 84	Sept. 84	>21	15	12	12
PR-1422 B-1/2	July 84	October 84	10	10	10	10
PR-1422 B-2	Sept. 84	Sept. 84	19	19	12	12
PR-1750 A-1/2	June 86	August 86	<6	<6	<6	<6
PR-1750 A-2	June 86	August 86	<6	<6	<6	<6
PR-1750 B-1/2	May 86	August 86	<6	<6	<6	<6
PR-1750 B-2	May 86	August 86	<6	<6	<6	<6
PR-1750 B-6	July 86	August 86	>18	18	12	<8

Table 17 Weight losses from sealant containers stored at 25°C

Contents*	Weight Loss (%)	
	17 days	280 days
Toluene, CaCO ₃	17.4	22.4
Toluene, CaCO ₃ (foil seal)		9.8
MEK, toluene, CaCO ₃	13.0	21.9
MEK, toluene, CaCO ₃ (foil seal)		12.0
MEK, CaCO ₃	2.4	19.6
MEK, CaCO ₃ (foil seal)		9.2
MEK, LP-32	0.05	1.2
MEK, toluene, LP-32	0.12	2.3
Toluene, CaCO ₃ , LP-32 [†]	0.1	1.9
PR-1422 A-2 Semkit	0.1	0.3
PR-1422 B-2 Semkit	-	0.06

* MEK = methyl ethyl ketone; solvent to CaCO₃ ratio of 30 to 100 w/w, solvent to LP-32 ratio of 10 to 100 w/w.

[†] toluene, calcium carbonate, LP-32 ratio of 10 : 30 : 60 w/w.

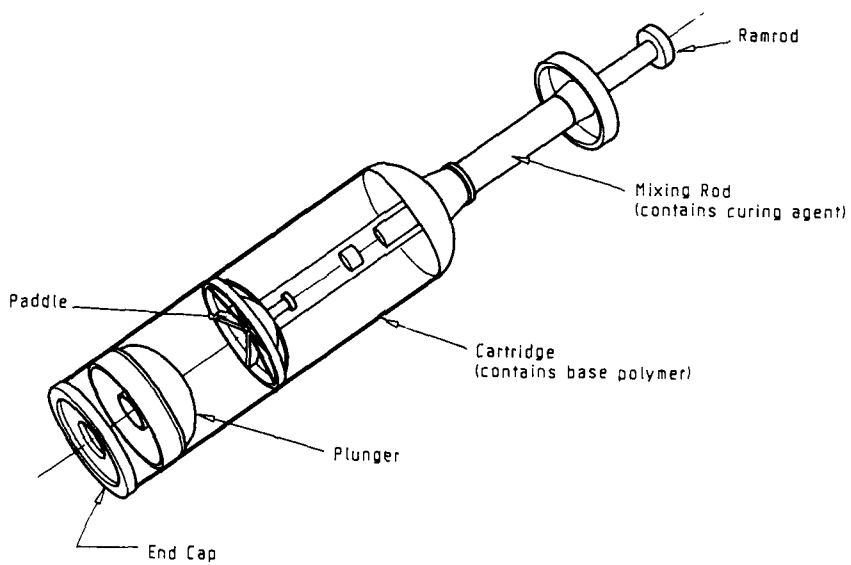


Figure 1 Schematic of the Semkit sealant packaging system.

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ABSTRACT

The storage performance of a range of PR-1422, PR-1436G and PR-1750 two part polysulfide aircraft sealants of A and B classes, packaged both in cans and Semkit form, has been surveyed. The sealants were separately maintained at temperatures of -16° , 2° , 13° and 25°C and changes in viscosity of the polymer base compound, cure rate, peel strength and application life were monitored over 26 months. Concurrent changes in thiol content of the liquid polymer in the base compound and concentrations of Mn(IV) or Cr(VI) in the cure pastes were also determined. Variations in activity of cure pastes with time were assessed using LP-32 as a standard polymer and changes in polymer base compounds were monitored by measuring cure rate with laboratory prepared reference cure pastes.

Low temperature storage extended storage life significantly. After maintenance at temperatures of 2° and below, the canned sealants still performed satisfactorily after two to three years storage. Most materials were procured several months after manufacture and with reduction of acquisition time further extension of the low temperature storage life could be expected. No significant storage differences between PR-1750 and PR-1422 sealants or the A or B classes were noted. Dichromate-based cure pastes were prone to lose solvent at higher storage temperatures and some dried pastes resulted. The main cause of failures was oxidation of the polymer base compound which led to surface skinning and was accompanied by a gradual drop in thiol content. Peel strength was unaffected by storage and the concentrations of Mn(IV) and Cr(VI) were little changed.

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