UNLIMITED

TR 77014

DR57346

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ROYAL AIRCRAFT ESTABLISHMENT

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Technical Report 77014

A CHEMICAL TREATMENT FOR MERCURY ACCIDENTALLY SPILLED IN AIRCRAFT

by

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Farnborough, Hants

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REPORT DOCUMENTATION PAGE

Overall security classification of this page

UNLIMITED

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1. DRIC Reference (to be added by DRIC)	2. Originator's Reference RAE TR 77014	3. Agency Reference N/A	4. Report Security Classification/Marking UNCLASSIFIED

5. DRIC Code for Originator 850100	6. Originator (Corporate Author) Name and Location Royal Aircraft Establishment, Farnborough, Hants, UK
5a. Sponsoring Agency's Code N/A	6a. Sponsoring Agency (Contract Authority) Name and Location N/A

7. Title A chemical treatment for mercury accidentally spilled in aircraft

7a. (For Translations) Title in Foreign Language

7b. (For Conference Papers) Title, Place and Date of Conference

8. Author 1. Surname, Initials Allsopp, H.J.	9a. Author 2 -	9b. Authors 3, 4 .... -	10. Date January 1977	Pages 29	Refs. 20
11. Contract Number N/A	12. Period N/A	13. Project	14. Other Reference Nos. Mat 313		

15. Distribution statement

(a) Controlled by – Unlimited

(b) Special limitations (if any) –

16. Descriptors (Keywords) (Descriptors marked * are selected from TEST)

Mercury*. Aluminium alloys*. Embrittlement*. Decontamination.

17. Abstract

Tests were made to determine the susceptibility of commercially pure aluminium, and of high strength Al-Zn-Mg-Cu and Al-Cu alloys to embrittlement by mercury. Commercially pure aluminium to BS L16 is not embrittled by mercury. DTD 5050B (Al-Zn-Mg-Cu) is very susceptible to mercury embrittlement; cracking occurred when the alloy was stressed in the short transverse direction at 5% of the 0.2% proof stress. DTD 5020A (Al-Cu) is more resistant to mercury embrittlement, although it cracked when stressed in the short transverse direction at 60% of the 0.2% proof stress.

A chemical technique using silver nitrate was developed to immobilise and render relatively harmless any elemental mercury accidentally spilled in aircraft. The corrosion and stress-corrosion hazards to alloys DTD 5020A and DTD 5050B, associated with silver nitrate and the products of its reaction with mercury, have been investigated.

F5910/1

RAE Form A143

UDC 669.791 : 669.715 : 539.56 : 620.19

⑱ DRIC ⑲ BR-57346

ROYAL AIRCRAFT ESTABLISHMENT

⑨ Technical Report 77014

Received for printing 31 January 1977

⑭ RAE-TR-77014

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SUMMARY

Tests were made to determine the susceptibility of commercially pure aluminium, and of high strength Al-Zn-Mg-Cu and Al-Cu alloys to embrittlement by mercury. Commercially pure aluminium to BS L16 is not embrittled by mercury. DTD 5050B (Al-Zn-Mg-Cu) is very susceptible to mercury embrittlement; cracking occurred when the alloy was stressed in the short transverse direction at 5% of the 0.2% proof stress. DTD 5020A (Al-Cu) is more resistant to mercury embrittlement, although it cracked when stressed in the short transverse direction at 60% of the 0.2% proof stress.

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Departmental Reference: Mat 313

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I INTRODUCTION

The natural oxide film on aluminium ennobles the metal, enabling it to exhibit good corrosion resistance. When ruptured the film reforms rapidly in the presence of an oxygen source and the absence of an aggressive electrolyte. The thickness of the natural oxide film on aluminium and its alloys is usually between 3 and 5 nm, but on as-rolled material it can exceed 10 nm. For corrosion to take place this film must be ruptured. When this occurs in the presence of elemental mercury, amalgamation will occur. Amalgamation will also occur in the presence of aqueous solutions of mercuric compounds: aluminium will reduce mercuric ions to the metal. The resulting amalgam will oxidise at the surface to produce aluminium oxide, or hydroxide and hydrogen in the presence of water. Fine needles of the hydrated oxide appear on the surface of the amalgam in the presence of moist air, leaving elemental mercury free to amalgamate with more aluminium[1]. The rate of evaporation of mercury is so low (the vapour pressure being about 70 mPa or 5×10^{-4} torr at 20°C) that it can remain in the vicinity of the aluminium surface for long periods of time, thus representing a considerable corrosion hazard.

The embrittlement of aluminium alloys by mercury is reported in a number of papers[2-16]. These show that high-strength aluminium alloys in the AA 2000 and 7000 series are susceptible to mercury embrittlement. Crack initiation occurs at the liquid metal/solid metal interface. The presence of mercury lowers the energy required to initiate a crack, and once initiated the mercury causes the crack to grow at faster rates and at lower stress levels, providing mercury is continuously available to the new surfaces. Fractures so produced are of a brittle nature, propagating either between or through the grains[11]. Crack velocities are quite high: rates in the region of 30 mm s^{-1} have been measured[10] compared with rates of 10^{-3} to 10^{-5} mm s^{-1} observed for stress corrosion cracking of aluminium alloys in the presence of halide ions.

Elemental mercury can find its way into military aircraft structures in several ways, *eg* broken mercury vapour lighting, broken manometers used for calibrating instruments, and broken instruments carried as freight. Methods for dealing with such incidents have been described[17] and rely mainly on seeing the mercury and physically removing it. Radiography can be used to locate mercury in inaccessible places. Mercury finding its way into such places could remain there, and flexing of the aircraft structure in the vicinity of the mercury could cause amalgamation of the structural aluminium alloys. Severe corrosion or embrittlement could then occur. One of the techniques recommended by the RAF for dealing with mercury contamination is the copper brush collector. The multi copper wire strands are first cleaned in nitric acid and then dipped into mercury. Amalgamation immediately occurs. The copper brush is then dipped into the spilled mercury which is drawn up the wire by capillary action. This use of copper indicated that a newly formed metal surface could react rapidly with mercury. The resulting amalgam should be a lesser hazard than mercury. Fresh metal surfaces will result from the reaction of mercury with salts of more noble metals, *eg*, copper, silver, gold. Several such reactions of mercury were considered as methods of converting it into compounds which would be less damaging to aircraft structures. The most promising was the reaction, reported by Ogg[18] in 1898, between mercury and an excess of silver nitrate, in which the latter was reduced and a silver/mercury alloy was formed. This Report describes an initial assessment of the reaction as a means of removing the potential hazard of elemental mercury spilled inside an aircraft structure. It also evaluates the corrosion and stress-corrosion of aluminium alloys in the presence of silver nitrate, and the mercuric salts and amalgam formed.

2 THE EMBRITTLEMENT OF ALUMINIUM ALLOYS BY MERCURY

2.1 The alloys and test pieces used

The aluminium alloys chosen for this investigation were to the Specifications DTD 5020A and DTD 5050B for plate material, referred to throughout this Report as 5020 and 5050. They were used in the form of 3.125mm diameter tensile test pieces cut so that stress could be applied in the short transverse direction in a constant tensile strain rig[19], similar to the Alcoa rig; 5050 was also fabricated into short transverse sheet tensile, 'C'-type test pieces (Fig 1). Some preliminary testing was done using aluminium and aluminium alloy sheet to the British Standards Institution Specification BS L16, BS L71 and BS L88, the latter clad alloy being used both as-received and with the cladding removed. These materials are referred to throughout this Report as L16, L71, L88 and unclad L88. They were used in the form of sheet tensile 'C'-type test pieces (Fig 1), machined so that the stress could be applied in the long transverse direction. The composition and tensile properties of the alloys are listed in Table 1.

2.2 The amalgamation of aluminium and its alloys

Four techniques were investigated.

2.2.1 A small area in the centre of a sheet tensile test piece was electropolished to remove the oxide, and onto this surface a small droplet of mercury was placed either before or after stressing.

2.2.2 A small glass cylinder filled with mercury was positioned in the centre of the gauge length of a sheet tensile test piece. An 0.6mm diameter drill was used to drill into the metal surface, through the pool of mercury. This technique has been described by Otto, *et al.*[8]. In some cases experiments were done with mercury and water or 5% w/v sodium chloride solution in the cylinder.

2.2.3 Sheet tensile test pieces were coated with Fortolac, a protective lacquer, leaving a bare area about 10 mm^2 along the gauge length which was flooded with a 2% w/v solution of mercuric chloride. Mercury salts react with aluminium to give elemental mercury and amalgamation with the reactive aluminium surface can be instantaneous.

2.2.4 Sheet tensile test pieces were immersed, through 20% w/v sodium hydroxide solution at room temperature for 1 min (to remove the oxide film), into mercury (1 min). The 5020 and 5050 Alcoa-type constant tensile strain test pieces were stressed in their frames using the technique previously described[19]. They were protected, together with their frames, by immersion in Crocell PL4, a transparent hot dip-applied coating conforming to CS 2486, leaving only the gauge length unprotected. Amalgamation of the test pieces was then achieved by passing the assemblies through sodium hydroxide into mercury (as for the sheet tensile test pieces).

2.3 The effects of stress

It was clear from the outset that the main problem was to ensure that there was wetting of the test pieces by the mercury. This was necessary before embrittlement could occur. Preliminary experiments were done using sheet tensile test pieces of L16, L71 and L88 both clad and with the cladding removed. Details are given in the Appendix and the results are summarised in Figs 2-4. This work indicated that (a) commercially pure aluminium (L16) was not embrittled by mercury, (b) the method, described in section 2.2.4, of passing the alloys through aqueous sodium hydroxide into mercury was the best method tried for wetting the alloys with mercury, (c) stress must be applied while the alloy is wetted with mercury for embrittlement to occur, (d) L88 was more susceptible to mercury embrittlement than L71, and (e) L88 was more susceptible when stressed in the short transverse than in the long transverse direction.

As a result of these preliminary experiments, tests were performed on short transverse tensile bar test pieces of 5020 and 5050 held at constant strain in Alcoa-type frames. When 5050, stressed at 5% of the 0.2% proof stress (PS), was amalgamated by passing the test piece and stressing frame through aqueous sodium hydroxide into mercury (as described in section 2.2.4), failure occurred within 10 min in duplicate experiments. It was not possible to apply accurately the minute strains to test at stresses below this figure. Similar experiments with two 5020 test pieces, stressed at 90% of the 0.2% PS, resulted in failures in less than 5 min. One of two test pieces stressed at 60% of the 0.2% PS failed in less than 10 min, the other survived for 24 h; and two test pieces stressed at 30% of the 0.2% PS survived 24 h. As in the tests using sheet tensile test pieces of L71 (see Appendix), it appeared that the mercury was rejected from the 5020 surface very rapidly, leaving a dark, powdery surface.

3 THE REACTION OF SILVER NITRATE WITH MERCURY

Silver nitrate is reduced by mercury and the resulting metallic silver is amalgamated. The stoichiometry of the reaction is not known but may approximate to the equation:

$$3Hg + 2AgNO_3 \rightarrow Hg(NO_3)_2 + 2AgHg \quad .$$

Thus 600 g of mercury would require about 340 g of silver nitrate to convert it into its amalgam plus mercuric salts. The phase diagram for silver-mercury[20] indicates intermetallic compounds containing 40 wt.% and 30 wt.% (55 and 45 molar per cent, respectively) of silver. Between these compositions no free mercury is present below 127°C, and above 40 wt.% silver no free mercury is present below 276°C. Temperatures above 127°C are unlikely inside an aircraft structure and, therefore, for most applications sufficient silver nitrate should be used to ensure the formation of an alloy containing over 30 wt.% silver.

Accidental spillage of mercury in an aircraft could involve the contamination of a considerable area of the structure. If aqueous silver nitrate were to be used, relatively large volumes of solution would be required to convert it into a silver amalgam and mercuric salts. As silver nitrate is an expensive, toxic material and a potential corrosion hazard, dilute solutions would be more acceptable for use in neutralising elemental mercury. Consequently, two concentrations were studied, namely 2% and 5% w/v.

Droplets of mercury varying in mass from 172 to 178 mg were added to 100 cm^3 quantities of 2% and 5% silver nitrate solution and allowed to react for times from 2 min to 17 h, without stirring, to simulate a practical situation where a droplet of mercury is inaccessible. The silver contents of the drops were determined gravimetrically during the experiment. The results are expressed graphically in Fig 5; the silver contents, expressed as a percentage by weight of the silver-mercury alloy, are plotted against the time of exposure in minutes. It can be seen that the uptake of silver in the case of the 5% solution was much faster and that the quantity of silver in the alloy had reached 30 wt.% after 30 min and 40 wt.% after 17 h, despite the absence of stirring, whereas in the 2% solution of silver nitrate the silver content of the mercury drops had only reached 30 wt.% after 17 h. A 5% silver nitrate solution was, therefore, chosen for this investigation to ensure rapid transformation of mercury to an alloy free from elemental mercury.

The extent to which 5% silver nitrate would react with mercury under conditions likely after spillage inside an aircraft structure was investigated. Two situations were envisaged. One where a mercury drop had lodged in a crevice and the other where small droplets of mercury lay dispersed over an extensive area on a flat surface. Two experiments were carried out to simulate these situations.

In the first experiment, a chemically-clean glass tube of 8mm internal diameter was drawn down to a fine capillary point and closed at that point. 276 mg of mercury was placed into the capillary and 25 cm^3 of 5% silver nitrate added above the mercury (about an eight-fold excess of silver nitrate). This was allowed to stand for 24 h and the amalgam then analysed for silver content. The second experiment involved a chemically-clean glass tray over which 400 mg of mercury was spread in the form of droplets of less than 0.5mm diameter. These droplets were covered with a 1mm layer of 5% silver nitrate (40 cm^3; about an eight-fold excess of silver nitrate). The system was left static and after 30 min and 24 h had elapsed, micro samples of the amalgam were analysed for silver content. The results of these two experiments were similar: the reaction of the first had gone well over half way to completion[20], the amalgam having a 28% by weight silver content which indicated a molar ratio of 0.72:1 of Ag:Hg; and that of the second about 70% to completion, the amalgam having silver contents of 33.7 and 35.2% by weight after 30 min and 24 h exposure respectively, or approximately equimolar amounts of silver and mercury. When mercury and an excess of silver nitrate (eight-fold) were stirred together for 24 h, the amalgam obtained was 48% by weight of silver, a molar ratio of 1.71:1 of silver:mercury.

4 THE EFFECT OF SILVER NITRATE ON ALUMINIUM ALLOYS

4.1 The reaction of silver nitrate with aluminium alloys

The reaction between silver nitrate and aluminium should result in the reduction of the silver nitrate to silver with the formation of aluminium nitrate:

$$3AgNO_3 + Al \rightarrow Al(NO_3)_3 + 3Ag \quad .$$

Initially, two materials were examined, L16 and 7178-T6 alloy in sheet form, the latter in the anodised condition and also with the anodic film removed. Coupons of the materials were placed into test tubes containing 100 cm^3 of 5% silver nitrate and left static for times up to 8 days at ambient temperature. The coupons were weighed at the outset and then at intervals of 1, 2, 4 and 8 days after they had been washed with distilled water and dried. The silver nitrate solutions were analysed at the end of the test period for aluminium in the case of L16, and magnesium, zinc and copper in the case of 7178-T6 alloy. The L16 sheet lost weight at a sensibly constant rate of about 8 g m^{-2} d^{-1}, whereas the anodised 7178-T6 lost only about 1.5 g m^{-2} d^{-1}, both over a period of 8 days. The 7178-T6 alloy from which the anodic film had been removed lost just under 11 g m^{-2} d^{-1} over 4 days which was similar to the rate of weight loss of the L16 test coupon during the first 4 days exposure (see Fig 6). The metal ions in solution were present in about the same ratios as the metals in the parent alloys (see Table 2).

Unstressed short transverse Alcoa-type test pieces of 5020 and 5050 were subjected to alternate immersion, each in a 1dm^3 bath of 5% silver nitrate at $27^\circ C \pm 0.5^\circ C$, the immersion time being for 10 min in every hour with 50 min drying time in air, for 28 days. In this time they suffered a weight loss of 7%, equivalent to an average decrease in diameter of about 2.7%. Subsequent measurement of the mechanical properties showed no loss either in tensile strength (TS) or in elongation.

4.2 The effects of stress

Alcoa-type short transverse test pieces of 5020 and 5050 stressed to 90% of the 0.2% PS were subjected to a 28 day period of alternate immersion, each in a 1dm^3 bath of 5% silver nitrate, as outlined in section 4.1. Both alloys survived this period unbroken in triplicate tests. Typical sections of test pieces after such treatment are shown, both etched and unetched, in Fig 7 at ×55 magnification. No evidence of microcracks was seen in any of the test pieces at ×500 magnification, although quite deep pits were present.

5 THE EFFECT OF SILVER NITRATE/MERCURY REACTION PRODUCTS ON ALUMINIUM ALLOYS

5.1 The effect of mercuric nitrate

Mercuric nitrate is formed from the reaction between silver nitrate and mercury, possibly according to the equation:

$$2AgNO_3 + 3Hg \rightarrow 2HgAg + Hg(NO_3)_2 \quad .$$

If this reaction represents the stoichiometry of the reaction, then a 5% silver nitrate solution would result in the formation of a 4.78% mercuric nitrate solution in a reaction to completion. A mercuric nitrate solution so produced would represent the extreme situation likely to occur when a deficiency of silver nitrate was used to treat a mercury spillage. Mercuric nitrate at this concentration was used for alternate immersion tests, done in triplicate each in a 1dm^3 bath, on stressed short transverse 5020 and 5050 Alcoa-type test pieces. Both alloys failed at 30% of the 0.2% PS and the failures were of a brittle nature. Fig 8 shows typical fractures of both alloys, Fig 8a being the 5020 surface and Fig 8b the 5050 surface both having the characteristic 'sugary' appearance of a brittle fracture. Fig 8c shows the 5020 fractured test piece as one unit and no reduction in diameter at the fracture is apparent, again demonstrating brittle fracture. Fig 8d shows one half of the 5050 test piece with no noticeable reduction in diameter, but with some attack of the fractured end itself. It was not possible to note the time to failure as both alloys were covered with a thick layer of orange mercury salt (possibly mercurous nitrate) which completely obscured the gauge length. The reduction in the diameter of the gauge length of unstressed short transverse test pieces of 5020 and 5050 over this period was 4%. Subsequent measurement of their mechanical properties showed a reduction in the TS of about 32% and in the elongation of 50%.

5.2 The effect of mercuric nitrate/silver nitrate mixtures

Stressed short transverse Alcoa-type test pieces of 5020 and 5050 were subjected to alternate immersion in a solution made by the addition of 30 g dm^{-3} of silver nitrate to a solution obtained from the reaction to completion of an excess of mercury with 5% silver nitrate solution. It was considered that this environment corresponded to an intermediate practical situation. The results were the same for both alloys. Three test pieces of each alloy survived unbroken when stressed at 90% of the 0.2% PS for 28 d; typical sections, etched and unetched, are shown in Fig 7 at ×55 magnification. No evidence of microcracks was seen at higher magnifications. Unstressed test pieces at the end of such treatment had lost about 2% of the diameter of their gauge length but their mechanical properties showed no deterioration either in TS or in elongation, similar to the results obtained in 5% silver nitrate (section 4.1).

5.3 The effect of mercury/silver amalgam

The other extreme situation envisaged was one in which a quantity of the silver amalgam was in contact with an aluminium alloy. Consequently the gauge lengths of stressed short transverse Alcoa-type test pieces of 5050 and 5020 alloy were surrounded with 10 g quantities of the silver/mercury alloy made by the reaction of mercury with an excess of silver nitrate. The amalgam *in situ* was moistened with 1 cm^3 of 5% silver nitrate solution and the mixture hermetically sealed to prevent drying out. Three 5020 test pieces survived unbroken for 28 d when stressed to 90% of the 0.2% PS. Three 5050 test pieces survived for 28 d when stressed to 30% of the 0.2% PS; one of two survived when stressed to 60% and those stressed to 90% of the 0.2% PS both failed. Typical sections (×76) of etched and unetched unbroken test pieces are shown in Fig 9.

6 DISCUSSION

For aluminium alloys to be embrittled by mercury or its salts the alloy surface must first undergo amalgamation. This is also true for accelerated corrosion of aluminium and its alloys which occurs in the presence of mercury. Various techniques were investigated to achieve the intimate contact of mercury and alloy surfaces which would lead to amalgamation; but the only one to give consistent results was passing the alloy through sodium hydroxide into mercury. Others[8] have been successful in using physical methods to remove the protective film from alloys in the presence of mercury in order to achieve amalgamation and, when the alloy was stressed, rapid embrittlement. However, in many experiments in which pre-stressed test pieces of L71 were slowly drilled through while immersed in mercury, ie conditions which should have continuously exposed fresh alloy surfaces to mercury, no evidence of embrittlement was obtained. Similarly, the action of mercuric chloride on pre-stressed test pieces of either L71 or L88 did not cause brittle failure. However, after exposure to mercuric chloride both alloys did show large but variable losses in mechanical properties when dynamically tested.

The unsuccessful attempts to amalgamate and embrittle the alloys by physical means indicated how unlikely it would be for spilled mercury or mercury salts to cause brittle failure of aluminium alloys in an aircraft structure under static load conditions. However, the possibility of mercury salts causing embrittlement could be much greater in a situation where stresses were fluctuating. Even with the potent and reproducible method of amalgamating through sodium hydroxide it was also reassuring to observe that the alloy had to be pre-stressed, or the stress applied within minutes of amalgamation for brittle fracture to occur.

The amalgamated surfaces on the Al-Cu and Al-Zn-Mg-Cu alloys rapidly rejected the mercury and thus removed the risk of local embrittlement. The Al-Cu alloys L71 and 5020 were also quite difficult to 'wet' with mercury after alkaline cleaning, and rejected mercury much more rapidly than did the Al-Zn-Mg-Cu alloys L88 and 5050 which were more readily 'wetted' by mercury. The observations now reported are not the only ones which are relevant. A far more dangerous situation could arise if chemically compounded mercury came in contact with a fatigue crack. It has been shown[11] that low stress intensity factor fatigue cracks can propagate very rapidly through 7075-T6 and 2024-T3 alloys when contacted with mercury. Thus, even though the rapid rejection of mercury from alloy surfaces in some circumstances is reassuring, the rejected mercury may still be available for further and possibly catastrophic attack if fatigue cracks are present.

Clearly, it is important that the last traces of mercury should be removed following any spillage within an aircraft structure. Physical methods are available for removing the greater part of any elemental spillage, and flushing with water will remove most, if not all, of any mercury compounds spilled. The removal of the last traces of these mercury sources can probably be achieved by using solutions of silver nitrate. The rate of reaction of mercury with silver nitrate is favourably high, even of mercury trapped in crevices, and the reaction produces a solution containing mercury salts and silver amalgam. The tests now reported on the corrosion of aluminium alloys by silver nitrate showed that the rate of corrosion, measured as a weight-loss rate, was only slightly greater than that observed in the presence of halide salt solutions. There was no observable stress corrosion hazard, in contrast to the well-known dangers involved in exposure of stressed aluminium alloys to salt solution. However, the mercuric salts formed by the reaction of mercury and the stoichiometric amount of silver nitrate caused a marked loss in mechanical properties of 5020 and 5050 alloy test pieces, subjected to alternate immersion in the unstressed condition. Cracking of test pieces of both alloys stressed to 30% of the 0.2% PS, in the short transverse direction, occurred during this test. However, mercuric salts in the presence of an excess of silver nitrate did not cause any loss in mechanical properties of unstressed material, nor any fracture of material stressed at 90% of the 0.2% PS in the short transverse direction. Thirdly, the silver amalgam caused cracking of 5050 alloy stressed at 60% of the 0.2% PS, but not of 5020 alloy stressed at 90% of the 0.2% PS, both in the short transverse direction.

Thus, the usefulness of silver nitrate as a means of chemically neutralising mercury was demonstrated but also some dangers were indicated. Should such a method be adopted, it would be necessary to take note of the possible dangers in any particular situation and adopt suitable safeguards. For example, to ensure that no danger of stress cracking would arise from the mercuric salts formed, an excess of silver nitrate should be present at all locations where mercury or its salts were found or even suspected. This would necessitate a reasonably accurate estimate of the maximum quantity of mercury present and its distribution. The use of more than a dm^3 of 5% silver nitrate per cm^3 of mercury is necessary to neutralize safely the effects of the mercuric salts generated. Even this ratio is only applicable if the distributions of the mercury and of the silver nitrate are such that the proportion of silver nitrate to mercury is not locally less than that suggested. The hazard of the silver amalgam is less than that of mercury or mercuric salts, and in the presence of large quantities of silver nitrate is probably negligible. However, any residual amalgam should be physically removed. This should be far easier than the physical removal of the mercury because the amalgam is in the form of a powdery solid which would readily be flushed away with running water or removed, when dry, by vacuum cleaning. Finally, silver nitrate itself is a corrodent which must be removed, by washing, after the silver nitrate/mercury reaction is judged to be complete, which may be as short as an hour or as long as 24 hours.

7 CONCLUSIONS

(1) High-strength Al-Zn-Mg-Cu alloy to DTD 5050B was very prone to mercury embrittlement and rapid failure occurred when exposed short transverse test pieces were stressed at 5% of the 0.2% PS.

(2) High-strength Al-Cu alloy to DTD 5020A was embrittled by mercury, rapid failure occurring when short transverse test pieces were stressed at 60% of the 0.2% PS. However, brittle fracture was not observed in short transverse test pieces wetted with mercury and stressed at 30% of the 0.2% PS.

(3) A chemical neutralising technique using 5% silver nitrate has been evolved to immobilise and render comparatively harmless elemental mercury spilled in aircraft. The method shows promise for the removal of small quantities of mercury.

(4) Further assessment is necessary to ensure that no other long-term corrosion hazard remains after such treatment.

Appendix

ATTEMPTS TO EMBRITTLE ALUMINIUM ALLOYS WITH MERCURY AND ITS SALTS
(see section 2.3)

The initial experiments were done in triplicate in a Hounsfield Tensometer using transverse L71 sheet tensile test pieces, pre-stressed at 80% of the 0.2% PS. The technique described in section 2.2.2 was used, drilling through mercury into the alloy while stressed. This did not produce failures within 18 h when the test pieces were stressed at 80% of the 0.2% PS, nor did the presence of water or of 5% sodium chloride around the mercury pool affect the results. After the period of sustained load the test pieces were strained to failure, which occurred between 89 and 96% of the 0.2% PS (see Fig 2). Attempts were then made to encourage the wetting of the test pieces, stressed to 80% of the 0.2% PS as before, using the technique described in section 2.2.1, electropolishing of the alloy before the application of elemental or combined mercury. No failures occurred in times up to 16 h. Similar results were obtained by drilling through the mercury pool in the presence of water or 5% sodium chloride. Subsequent testing to failure revealed a slight variation in the residual strength. For those test pieces drilled through mercury in the presence of 5% sodium chloride failure occurred at 82% of the 0.2% PS, whereas those drilled through mercury alone, or with mercury plus water, failed at 94 and 96% of the 0.2% PS respectively. When drilling was done through a solution of 2% mercuric chloride into three test pieces pre-stressed at 80% of the 0.2% PS, failure did not occur in up to 18 h. Subsequent testing to failure produced residual strengths of 87% of the 0.2% PS (see Fig 2).

As controls, triplicate 'as-received' test pieces stressed to 80% of the 0.2% PS, were drilled through in the absence of mercury or mercuric chloride solution. Subsequent tensile testing resulted in failure at 94% of the 0.2% PS of an as-received test piece (see Fig 2). Thus it is highly probable that the reduction in residual strength of the test pieces which had been drilled through a pool of corrodent was almost entirely caused by the loss of metal, and that corrosion had a very minor effect.

Triplicate transverse test pieces of L71 in the as-received condition were exposed to mercury droplets, without drilling and while stressed to 80% of the 0.2% PS. No failures occurred in times up to 65 h, and straining to failure indicated a residual strength of 109% of the 0.2% PS. Attempts were made, in triplicate, to encourage the wetting by mercury of the test pieces by electropolishing a small area (see section 2.2.1) onto which the mercury was placed while the test pieces were stressed to 60% of the 0.2% PS. No failures occurred within similar times but some variations occurred in the residual strength: test pieces failed between 82 and 109% of the 0.2% PS. This variation disappeared when similarly treated test pieces were left for the same time, rinsed with 5% silver nitrate and tested to failure: the residual strength was 103% of the 0.2% PS. No failures occurred in times up to 70 h when 2% mercuric chloride was substituted for mercury on as-received pre-stressed test pieces. Variations in the residual strength were noted, depending on the pre-stress value. A test piece stressed for 70 h at 40% of the 0.2% PS in the presence of 2% mercuric chloride, subsequently failed at about 45% of the 0.2% PS. Others pre-stressed at 60%, 70% and two at 80%, subsequently failed at 64%, 82%, 97% and 104% of the 0.2% PS.

The difference between the residual strengths of the as-received test pieces treated with mercury alone (109% of the 0.2% PS), and those electropolished prior to exposure to mercury (80-109% of the 0.2% PS) may be related to the pre-stressing value of 80% of the 0.2% PS for the former and 60% for the latter. This suggests that attack was accelerated by the exposure of fresh surfaces of metal during testing to failure. This effect is also evident with as-received test pieces treated with 2% mercuric chloride when stressed between 40% and 80% of the 0.2% PS for several hours, after which they failed ultimately at stress levels between 45% and 97% of the 0.2% PS (Fig 2).

In all of the above tests in which mercury or mercuric chloride was used, wetting (if at all) of the test piece by elemental mercury was of very short duration indeed. The mercury was rapidly repelled from the surface forming spheres of about 0.5mm diameter or less, some of which actually 'jumped' from the surface which quickly became dark and powdery in appearance; this surface presumably consisted of the alloying elements which do not amalgamate with mercury[12].

The results of a few tests made using L16, either as-received or after electropolishing as in section 2.2.1, were in marked contrast to those obtained for L71. L16 test pieces which were subjected to straight tensile tests, or left at stresses up to 100% of the 0.2% PS, were rapidly wetted by the mercury and the characteristic 'trees' of hydrated aluminium oxide grew on the mercury. Despite this, after 18h exposure both the elongation and the TS of the L16 were unaffected, thus confirming earlier work which showed that commercial purity aluminium is not embrittled by mercury[8].

At this stage of the work it was decided to seek an alloy more susceptible to mercury embrittlement and also to try to improve the amalgamation technique.

It had been reported[8,13,14] that aluminium casting alloys containing zinc and magnesium were much less resistant to mercury corrosion than those containing copper and silicon. Al-Zn-Mg-Cu alloys in sheet and plate form were therefore investigated to see whether they were more susceptible to mercury attack than Al-Cu alloys. Preliminary work was done using L88 both as-received (clad) and with the cladding removed. Clad transverse sheet tensile test pieces were amalgamated using the sodium hydroxide/mercury technique (see section 2.2.4), and mechanically tested. For five test pieces failure occurred between 60% and 74% of the 0.2% PS (see Fig 3). During this series of tests it was noted that the mercury attack took place at the edges of the test pieces more than on the cladding. Furthermore, mercury attack was much more evident at the interface between the cladding and the Al-Zn-Mg-Cu alloy. This effect was probably due to the tunnelling effect of the mercury at this interface, the diameter of the tunnel being small enough to retain the mercury and thus inhibit any self-healing which otherwise could have occurred. Similar test pieces, with the cladding removed, were amalgamated using 2% mercuric chloride while stressed at 10% of the 0.2% PS. In all of the five tests the stress was raised by 10% increments to 100% of the 0.2% PS, mercuric chloride being replenished on the surface of the test piece after each increase in stress. They were then stressed to fracture after 1 and 20h exposures and failed at between 104% and 109%, and 77% and 91% of the 0.2% PS, respectively. The results are shown in Fig 3 where it can be seen that the test pieces held at 100% of the 0.2% PS for 20 h failed before that figure on mechanical testing. This again suggests that, during straining to failure, the fresh metal surfaces exposed as the oxide fractures can react more readily with mercury.

Mechanical testing of short transverse sheet tensile test pieces of 5050, less than 1 min after being amalgamated while unstressed by mercury after electropolishing, led to failure at stresses varying from 76% to 120% of the 0.2% PS in six experiments (see Fig 4). Test pieces pre-stressed to 70% of the 0.2% PS and then amalgamated with mercury after electropolishing failed either within 10 s to 6 min, or survived unbroken for 22 h. Test pieces amalgamated using the sodium hydroxide/mercury technique (see section 2.2.4) and stressed for 1 h at values between 3% and 6% of the 0.2% PS failed on subsequent mechanical testing between 78% and 115% of the 0.2% PS. Those tested immediately after amalgamation failed at values between 8% and 13% of the 0.2% PS and others, flooded with silver nitrate after stressing commenced, failed at similar values. However, test pieces similarly amalgamated and subjected to the 5% silver nitrate wash followed by an alcohol rinse *before* stress was applied, failed at between 94% and 115% of the 0.2% PS. Fig 4 summarizes all of the results obtained on short transverse sheet tensile test pieces of 5050, five of which were used in each experiment.

Table 1

THE NOMINAL COMPOSITIONS AND TENSILE PROPERTIES OF THE MATERIALS USED

Material	Nominal composition - wt.%							Tensile properties		
	Cu	Mg	Zn	Si	Cr	Mn	Al	Direction	0.2% PS (MPa)	TS (MPa)
BS L16 sheet							99.0	Long transverse	103	140
BS L71 sheet	4.4	0.7		0.7		0.6		Long transverse	448	488
DTD 5020A plate	4.4	0.7		0.7		0.6		Short transverse	403	446
BS L88 sheet	1.6	2.5	5.8		0.15			Long transverse	420	526
DTD 5050B plate	0.9	2.7	5.7		0.16			Short transverse	446	529

Table 2

THE EFFECT OF IMMERSION OF ALUMINIUM ALLOY COUPONS IN 100 cm^3 OF 5% SILVER NITRATE SOLUTION

Alloy	Coupon surface area (cm^2)	Time of immersion (days)	Weight loss of coupon (mg)	Rate of weight loss of coupon ($g\ m^{-2}\ d^{-1}$)	Analysis of silver nitrate solution at end of test for metal content other than silver		Alloy composition
					Total weight (mg)	Composition	
L16	50	8	317	7.9	299	>99% Al	>99% Al
7178-T6 (anodised)	37.5	8	44.5	1.5	46	Zn - 6.2% Mg - 2.7% Cu - 1.4%	Zn - 6.8% Mg - 2.7% Cu - 2.0%
7178-T6 (anodising removed)	37.5	4	164	10.9	143	Zn - 7.4% Mg - 2.6% Cu - 1.3%	Zn - 6.8% Mg - 2.7% Cu - 2.0%

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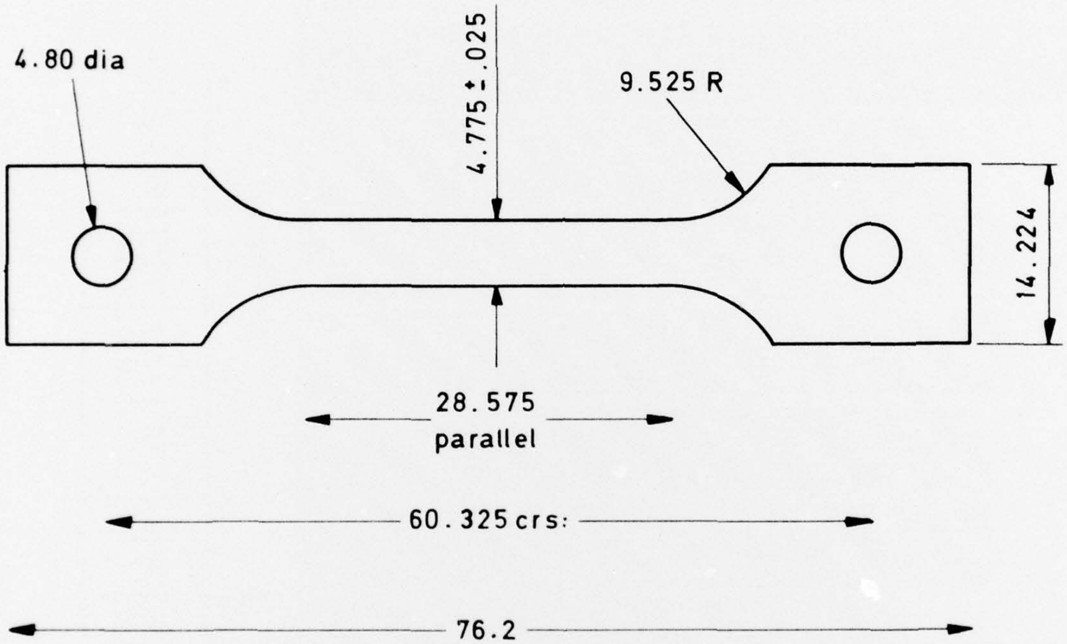


Dimensions in mm
Scale 2:1

Fig 1 'C'-type sheet tensile test piece

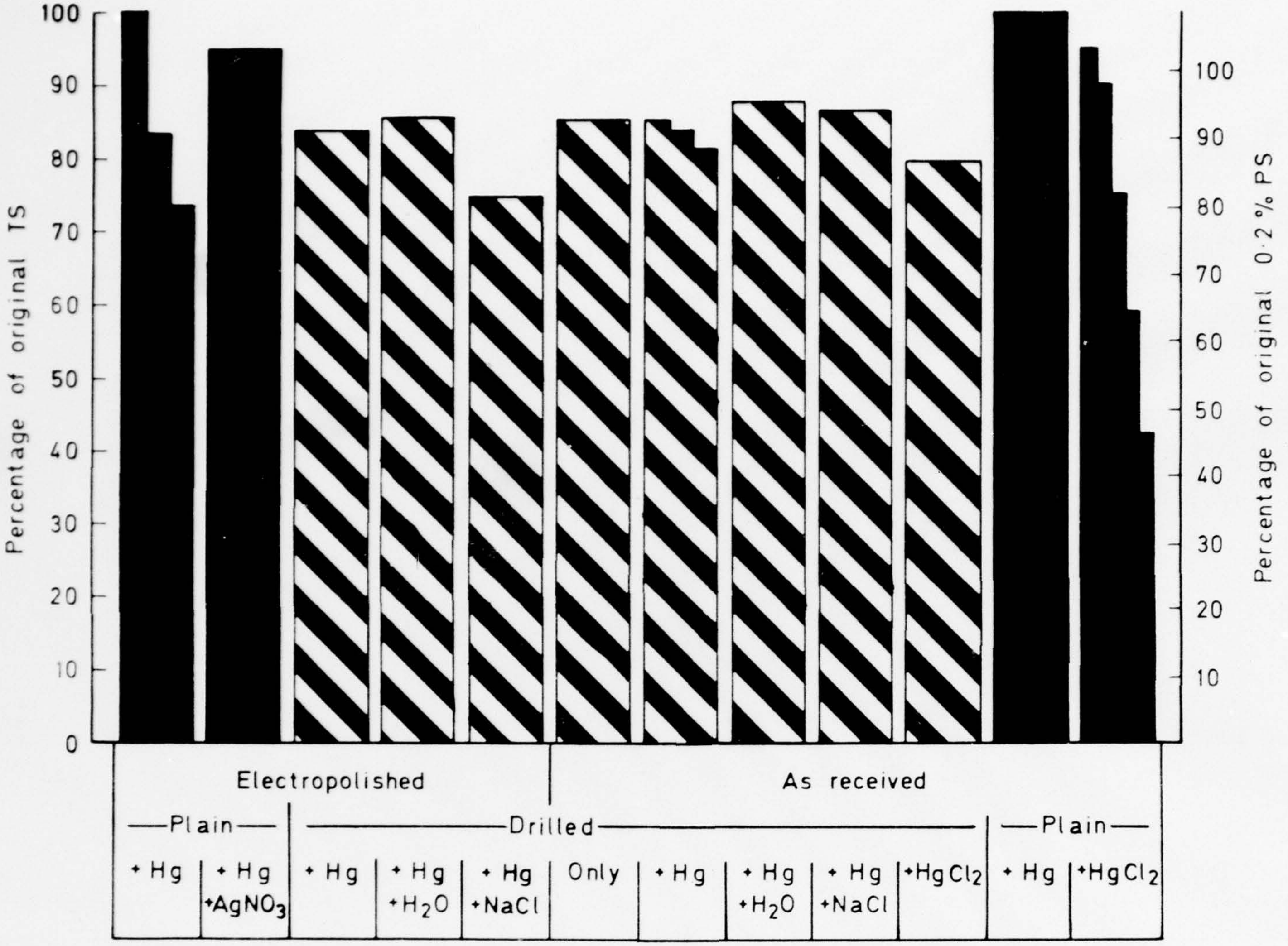


Fig 2 L71 'C'-type long transverse test pieces. Residual strength after exposure to mercury environments while stressed at up to 80% of 0.2% proof stress

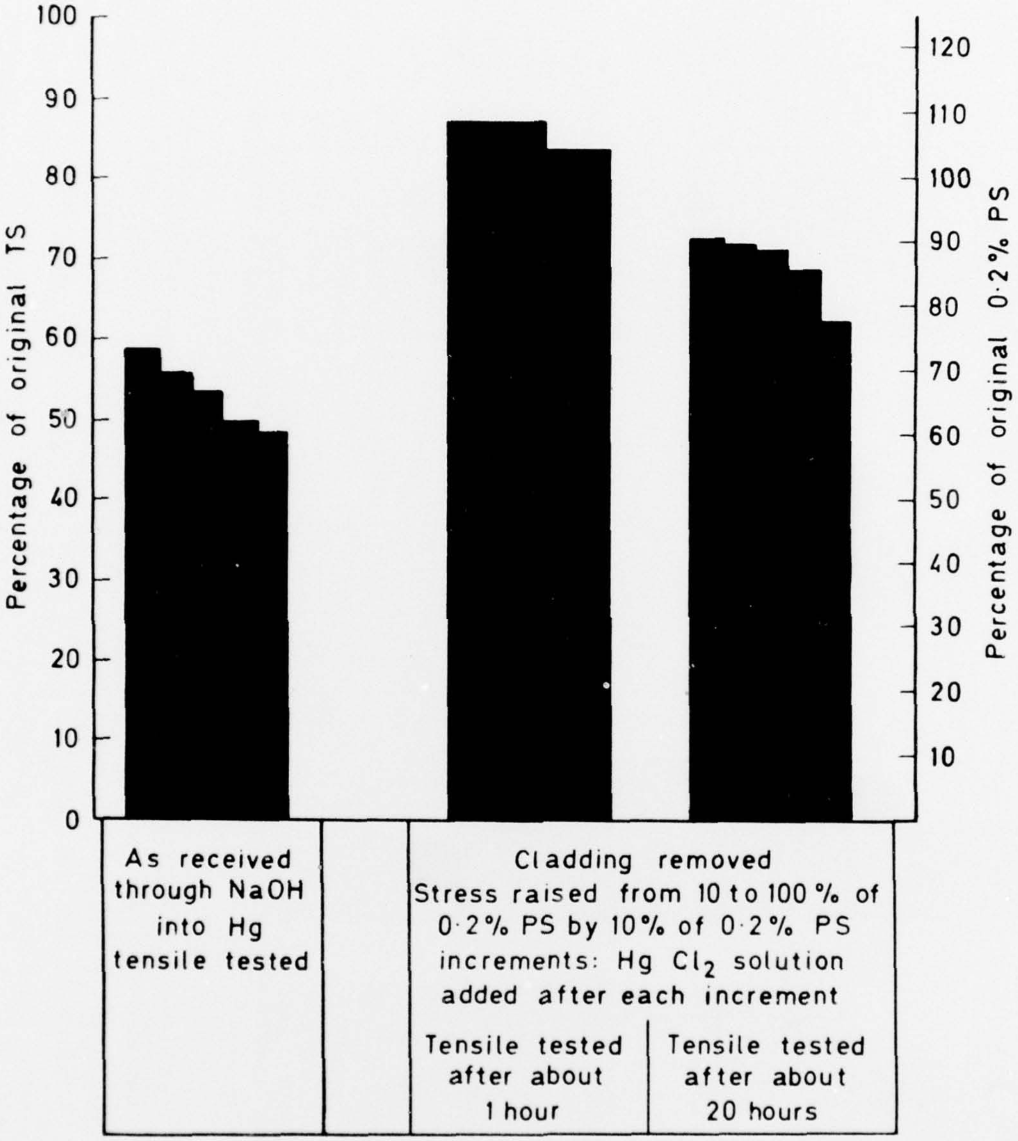


Fig 3 L88 'C'-type long transverse test pieces. Residual strength after exposure to mercury environments

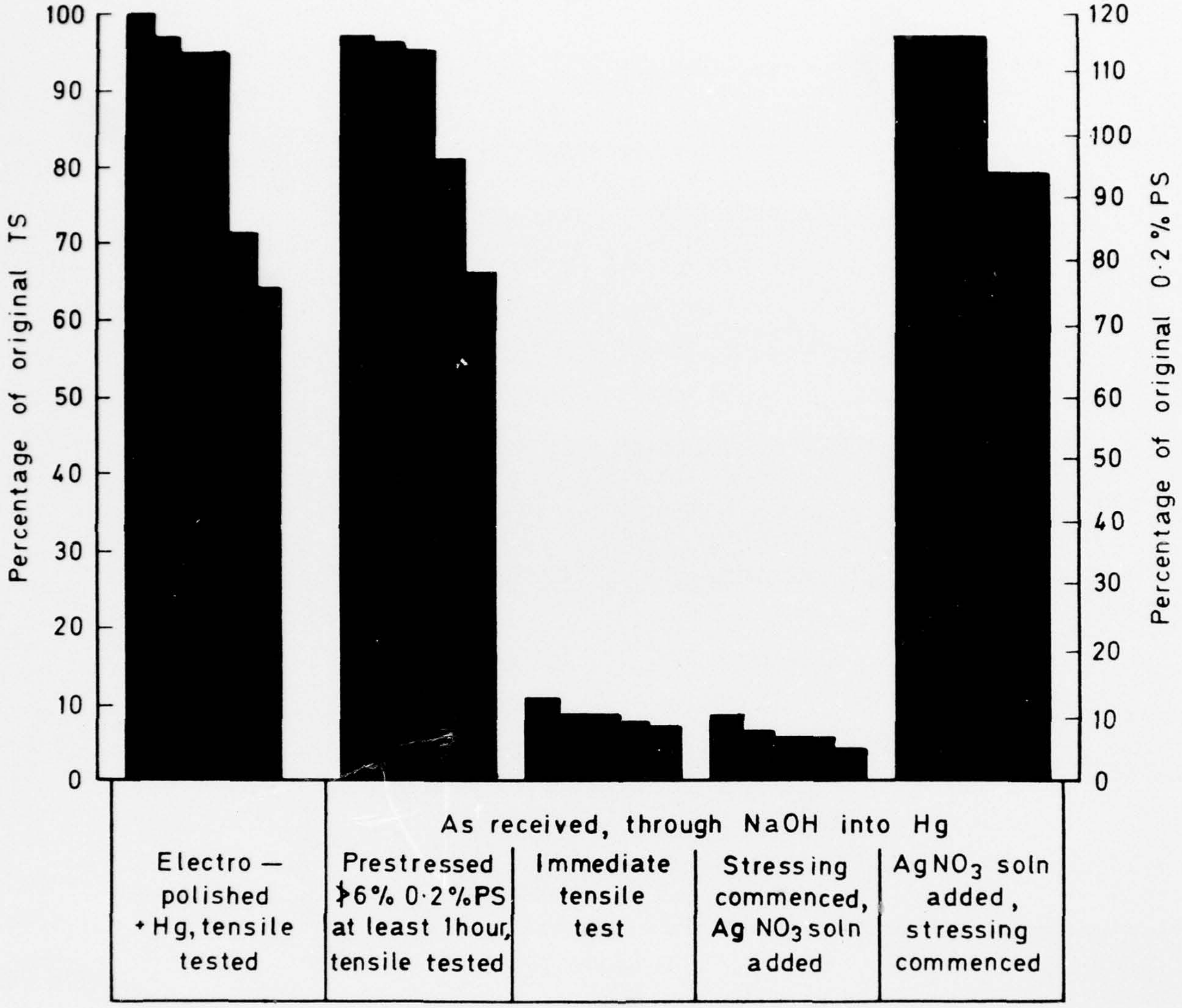


Fig 4 DTD 5050 'C'-type short transverse test pieces. Residual strength *after exposure to mercury*

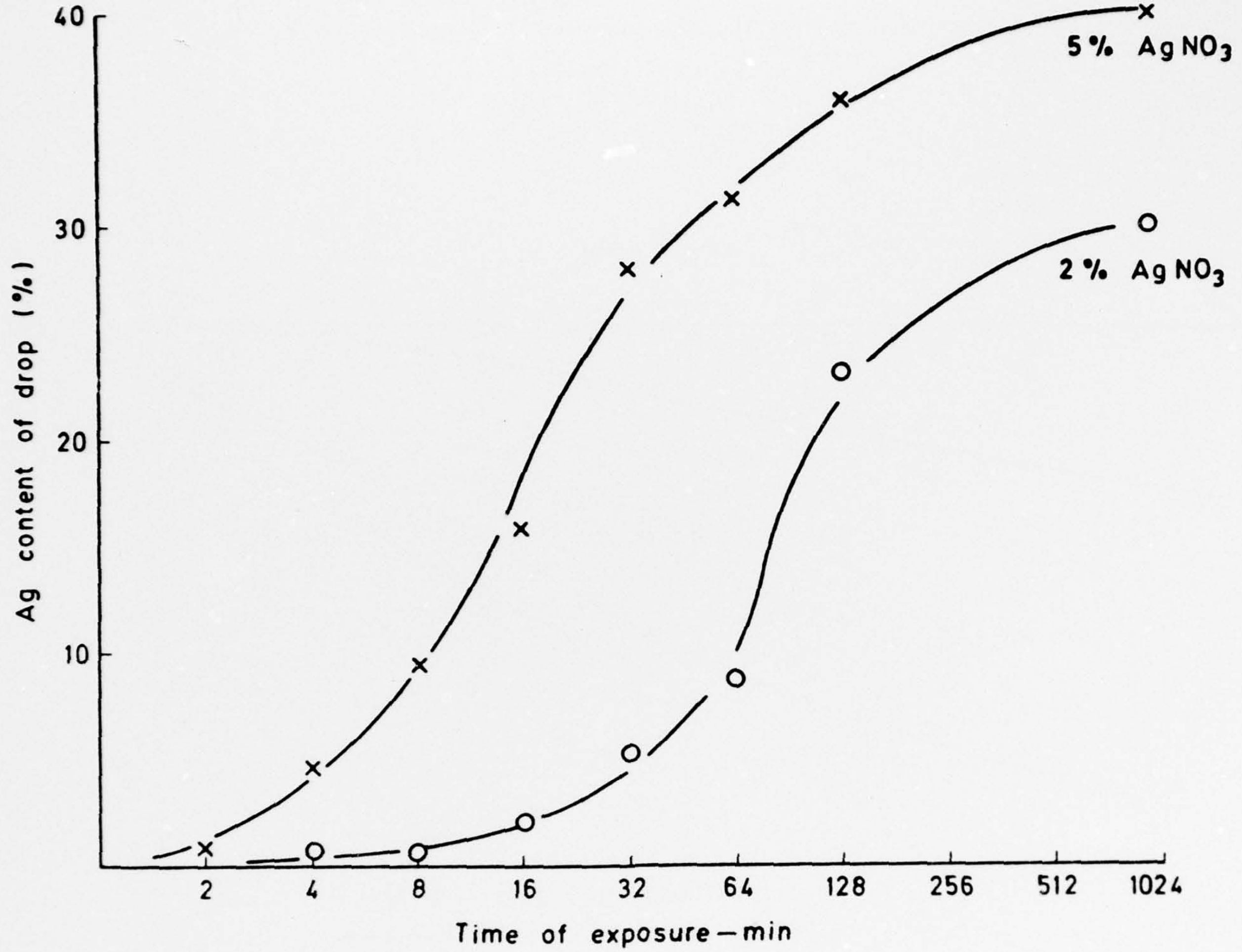


Fig 5 Uptake of silver by about 175mg mercury from 100 cm^3 quantities of silver nitrate solution

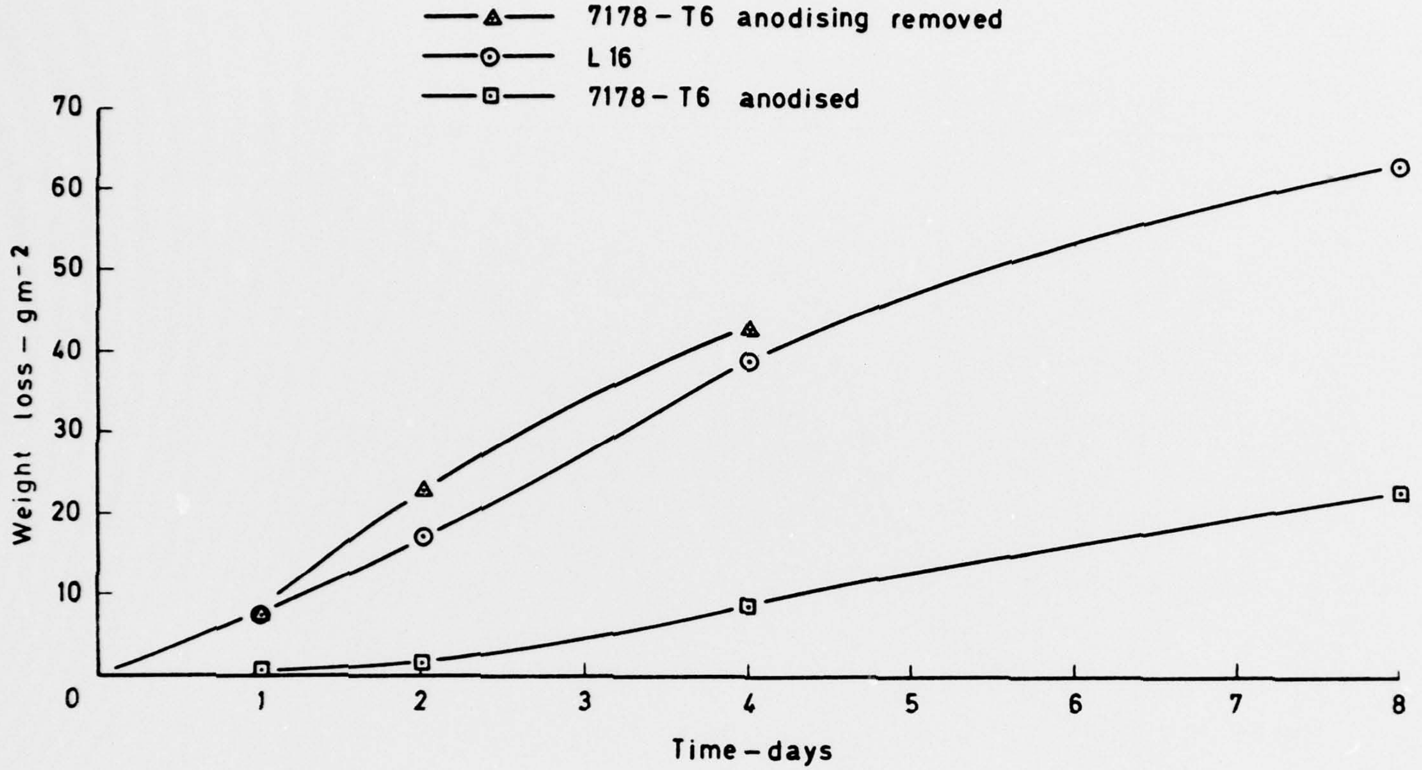
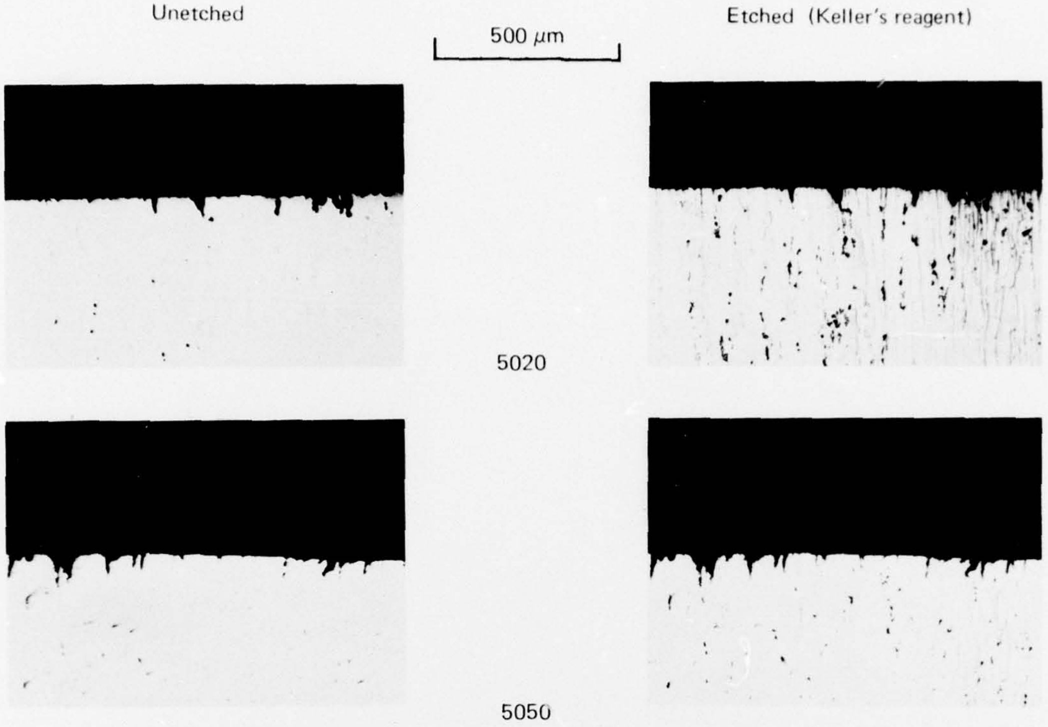
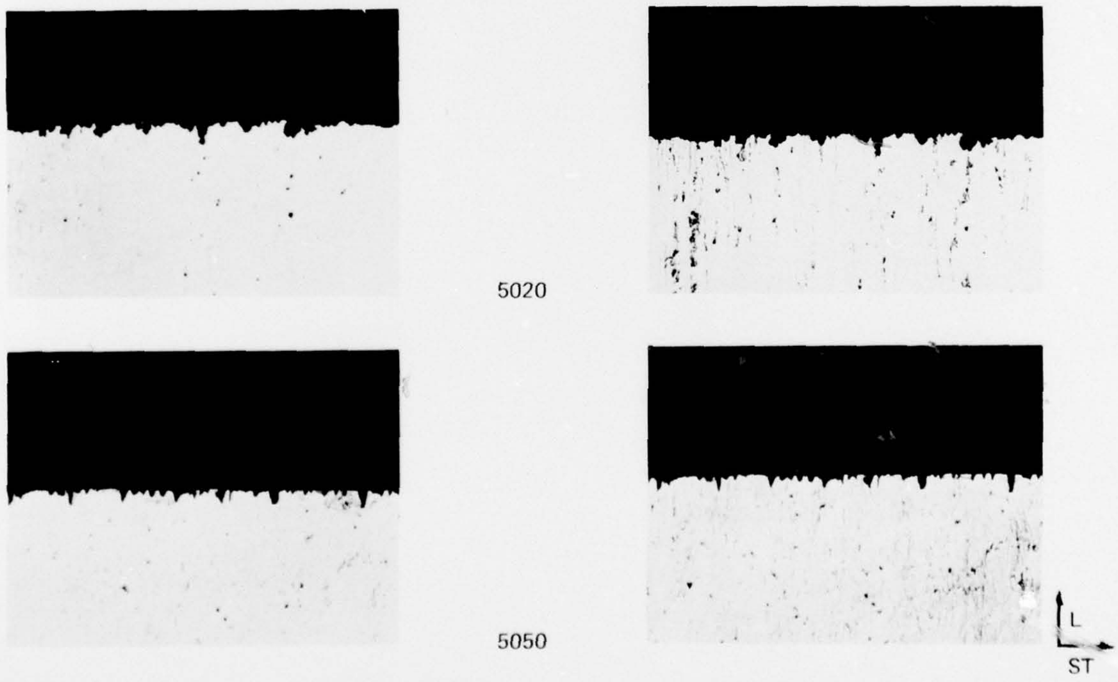


Fig 6 Weight loss from aluminium or aluminium alloy sheet when immersed in 5% silver nitrate solution

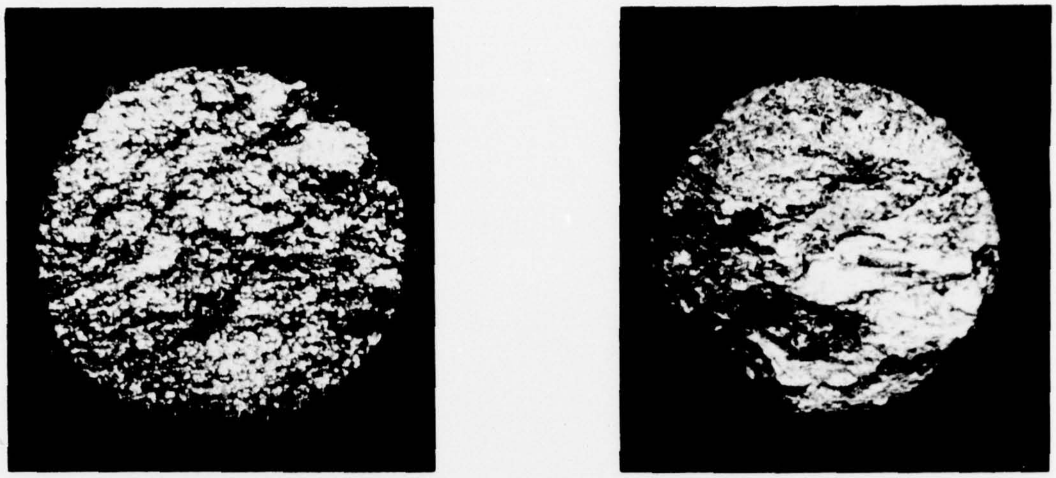


5% w/v silver nitrate solution



Silver nitrate/mercuric nitrate mixture

Fig 7 Test pieces stressed at 90% of 0.2% PS exposed for 28 days to alternate immersion in silver nitrate, and in mixed silver and mercuric nitrate solutions. L/ST sections

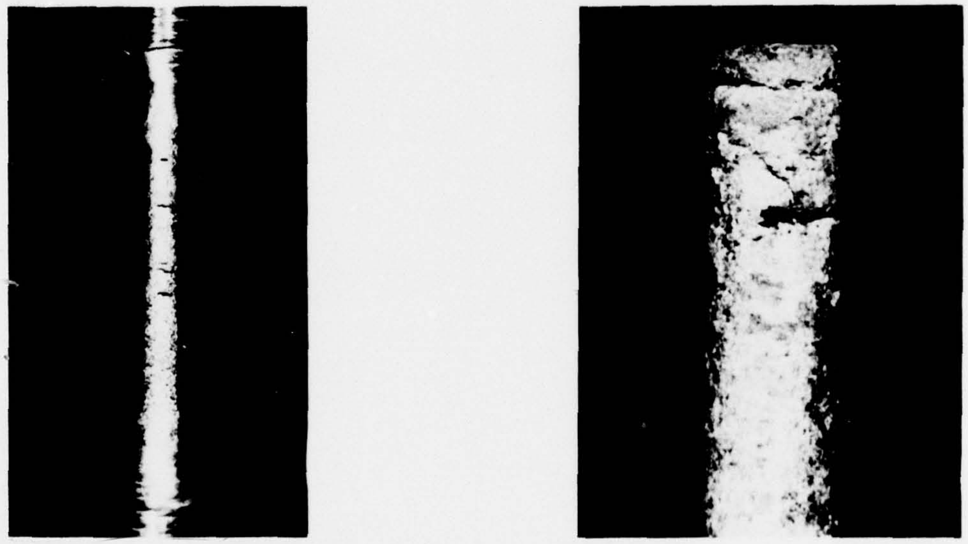


a approx x16

b approx x16

DTD 5020

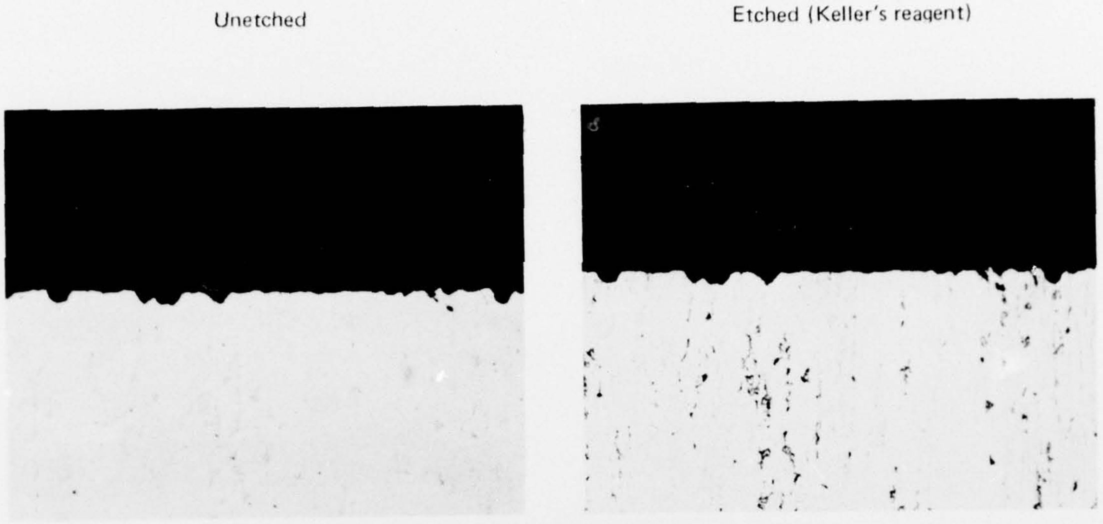
DTD 5050



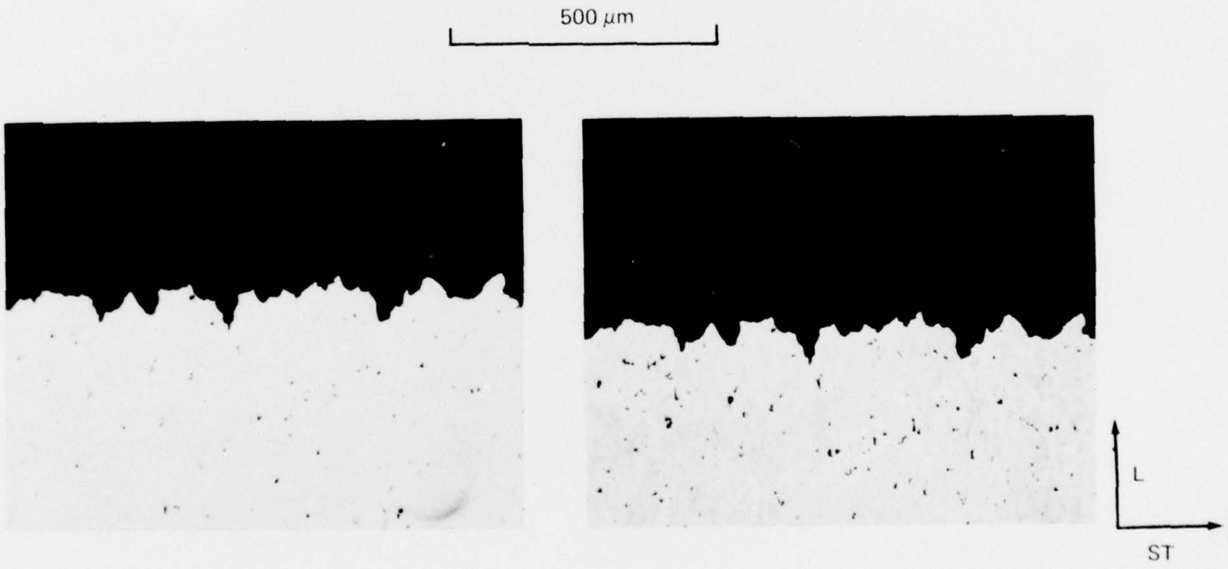
c approx x1.6

d approx x6

Fig 8 Fractured test pieces of 5020 and 5050 after exposure to Al in a solution of 4.78% mercuric nitrate for 28d showing a and b fracture surfaces: c and d surface appearance of test pieces after cracking had occurred



5020 stressed at 90% of 0.2% PS



5050 stressed at 30% of 0.2% PS

Fig 9 28 day exposure to moist silver-mercury alloy. L/ST sections