A032270

TR 76063

MAY

1976

ROYAL AIRCRAFT ESTABLISHMENT

TECHNICAL REPORT 76063

THE CORROSION RESISTANCE AND PAINT ADHESION PROPERTIES OF CHROMATE CONVERSION COATINGS ON ALUMINIUM AND ITS ALLOYS

by

H. J. Allsopp
J. B. Doble
V. C. R. Mcloughlin

PROCUREMENT EXECUTIVE, MINISTRY OF DEFENCE
FARNBOROUGH, HANTS

UNLIMITED

UDC 669.71 : 669.715 : 620.197.3 : 669.018.8 : 669.718 :
620.197.6 : 661.876.2 : 620.179.4

ROYAL AIRCRAFT ESTABLISHMENT

(9) Technical Report 76063 (14) RAE-TR-76063

Received for printing 25 May 1976

(6) THE CORROSION RESISTANCE AND PAINT ADHESION PROPERTIES OF CHROMATE CONVERSION COATINGS ON ALUMINIUM AND ITS ALLOYS

(14) DRIC

(11) BR-53655

by

(10) H. J. Allsopp
J. B. Doble
V. C. R. McLoughlin

(11) May 76

(12) 55p.

SUMMARY

A non-proprietary process for the chromate conversion coating (chromate filming) of aluminium and its alloys has been evaluated with respect to both corrosion resistance of, and paint adhesion to, the chromate films. The process involves immersion of the metal in an aqueous chromic acid/sodium dichromate/sodium fluoride solution for three minutes at 30°C. Iridescent, yellow-coloured films result. Alternative times and temperatures of immersion, pretreatments of the metal, washing and drying of chromate-filmed test pieces, and modes of application were examined. The chromate film thicknesses were measured and their corrosion resistance compared. Except for thin films (less than 50nm) corrosion resistance did not vary markedly with thickness. Comparisons were also made with two proprietary processes and no major differences were found in corrosion resistance or paint adhesion properties of the different chromate films. Of four methods used for assessing corrosion resistance, exposure to continuous 5% neutral salt fog was the best, and paint adhesion was evaluated by using two British Standards Institution test methods. The findings in this Report will be used as the basis for a Defence Standard for chromate conversion coatings for aluminium and aluminium alloys.

Departmental Reference: Mat 288

D
RECEIVED NOV 4 1976
D

10450

CONTENTS

1 INTRODUCTION

Chromate conversion coatings are used on aluminium and its alloys either alone or in conjunction with suitable paint schemes as a corrosion prevention measure. It is generally accepted that these coatings alone are less effective than anodic films in preventing corrosion, but they are cheaper and easier to apply. Also they have fairly low electrical contact resistances[1], in contrast to anodic films which are good insulators. It is possible[1] to spot weld directly onto chromated aluminium surfaces. They have been used in the past as an anti-corrosion treatment to the internal surfaces of aircraft structures not exposed to corrosive environments. Present requirements for UK service aircraft allow the use of chromate filming of aluminium alloys only as a basis for an approved paint scheme. In this application they provide a uniform surface pretreatment with good paint adhesion. Chromate filming treatments may be used for repair of damaged anodic films, and as the anti-corrosion treatment on the internal surfaces of sealed honeycomb structures.

Conversion coatings are formed when the nature of the metal surface is altered by chemical reaction. In the case of aluminium and its alloys the most widely used coatings are formed by reaction with solutions containing hexavalent chromium salts[2]. Ideally, a continuous gel-type film forms at the interface, the metal surface is oxidized, part of the reaction product remaining in the film which will contain chromium salts. During the process about 100nm of metal may be lost[3] and a coating of similar thickness will form. Thicker or thinner coatings, and commensurate metal losses, result from longer or shorter treatment times. The protective nature of the coatings is probably both physical and chemical: the gel-like structure acts as a barrier to corrodents, and leachable chromium-containing compounds in the film inhibit corrosion at breaks in the film. Chromate ions are excellent corrosion inhibitors and it is not unreasonable to expect them to be the effective species in the films. However, the chemistry involved in the formation of chromate coatings is not well understood and attempts to analyse the coatings indicate that chromium is present mainly in the trivalent state[3].

The most widely used class of chromate filming compositions are based on chromic acid with the addition of catalysts or accelerators: fluorides, ferricyanides, nitrates, and sulphates have been employed for these purposes[2]. The catalyst or accelerator increases the rate of attack on the aluminium surface, probably by the formation of soluble aluminium salts which may to some extent be incorporated in the resulting films. Many commercial processes employ immersion of the part to be treated in the coating solution (controlled between pH 1 and 3) at or slightly above ambient temperature for a few minutes. It is important to pretreat the part to remove any gross oxide film. After coating, the part is usually rapidly washed and dried to prevent local over-treatment of the surface by residual coating chemicals. Over-treatment of an aluminium surface, which can occur if it is left in the coating solution for too long at too high a temperature or in an over-concentrated solution, results in powdery films possessing poor corrosion resistance. Under-treatment conversely results when over-diluted solutions are used, when time of treatment is too short, or the solution temperature is too low; the films obtained can be patchy and very pale in appearance, with poor corrosion resistance. Treatment under optimum conditions yields films characterized by a golden-yellow and often iridescent appearance which are not readily detached from the aluminium surface[1,2].

It is important that chromate filming should result in a surface which has reasonable corrosion resistance and excellent paint adhesion properties. It is possible to increase corrosion resistance at the expense of paint adhesion by the simple expedient of producing thicker chromate films. The use of chromate filming in the aircraft industry is now very largely related to subsequent application of paint schemes, and it is therefore important that any filming process used should not sacrifice paint adhesion properties. There is no Defence Standard for chromate filming of aluminium and its alloys, although there are several proprietary processes approved in the DTD 900 series. In order to establish a Standard, it was decided that an open process should be investigated and optimized to give satisfactory chromate films. Tests related to corrosion resistance and paint adhesion would be devised and these would be required of any proprietary process also. This Report describes the experimental work performed to establish the required Defence Standard.

2 THE MARCHAND PROCESS

In 1961 a chromate filming process was described by Marchand[1] based on immersion of chemically-cleaned aluminium alloys in an aqueous solution of chromium trioxide (3.5 - 4.0g dm^{-3}), sodium dichromate (3.0 - 3.5g dm^{-3}), and sodium fluoride (0.8g dm^{-3}) for 3 minutes at 30°C. This produced chromate films on 99% aluminium, Al-Si (BS L33), Al-Cu-Mg-Si-Mn-Fe (HS14), and Al-Mn (NS3 and S1) alloys with corrosion resistance (in high humidity, salt spray environments) at least equal to those obtained from three proprietary processes and comparable with that of anodic films. The coatings proved to be good bases for enamels and showed low electrical contact resistance. However, they were unsuitable for application in the radio industry because the yellow appearance of the films did not match other finishes being used, and they tended to be iridescent and uneven in appearance.

It was decided to adopt the Marchand filming process as the basis for the open process required for the publication of a Defence Standard. The effects of variations on the basic process on the properties of the resulting films would be studied, and conditions established which would give films with reasonable corrosion resistance coupled with good paint adhesion. Comparison would be made with approved commercial processes.

2.1 Materials

Chromate coatings are applied to a wide range of aluminium alloys in aircraft and weapons systems. With modern methods of construction based on machining from plate both clad and unclad alloys are filmed. It was decided to use four alloys representative of the materials used: firstly, BS L16 commercially pure (99%) aluminium sheet; secondly, BS L71 Al-Cu-Mg-Si-Mn alloy sheet; thirdly, BS L88 a clad Al-Zn-Mg-Cu-Cr *alloy sheet used with the cladding* removed by machining and lastly, BS L33 Al-Si as 3mm thick castings and used either as-cast or with one face ground. The alloys were cut into test pieces either 100 × 25mm or 100 × 50mm with a 3mm diameter hole for supporting them during chromate filming.

2.2 Methods of evaluation

Adhesion of chromate films was assessed by rubbing the coating with a filter paper (Whatman No.40). The amount of material transferred, as judged by the staining of the filter paper, was taken as a measure of the adhesion; the test piece was also examined to ensure that the film had not been completely removed at any point. Appearance was judged on evenness rather than colour although it is generally agreed that good quality chromate films should be a golden-yellow colour[2]. Metal loss during filming, and thickness of the films were determined by weight differences before and after the various stages in the filming process. Weight differences of between 0.1 and 6mg were obtained for test pieces weighing between 10 and 20g. However, the weighings were only accurate to ±0.1mg and the weight differences observed could be in error by up to 100% for the smallest differences and up to 20% for average differences. Chromium contents of the films were determined by analysis of the dissolved films (see Appendix A).

Corrosion resistance of the different chromate filmed test pieces was assessed by various methods, the most useful and extensively used method being exposure to a continuous 5% neutral salt fog[4] at 35°C for 30 days. Two other laboratory tests were also used: exposure to the ARE salt-droplet test[5], described in part 2 of BS 1391, in which test pieces are sprayed once daily with synthetic sea-water in a high humidity environment for 30 days; and alternate immersion in 3.5% neutral salt solution (10 minutes immersed followed by 50 minutes drying) at ambient temperature, based on a stress corrosion test method[6]. Test pieces were also exposed for up to 1 year to two natural environments. A rural site located within RAE was used, with the test pieces held at an angle of 45° to the vertical, facing south, and about 1m above a concrete surface. Two marine sites were used: one was located above the foreshore of an inlet on the east side of Hayling Island, remote from industrial pollution, with the test pieces 1.5m above normal high tide level and over water for about 4 hours each day; the other was the Central Dockyard Laboratory site at Eastney where the test pieces were approximately 100m from the high water mark.

In the evaluation of chromate film properties, and subsequent evaluation of proprietary processes and paint adhesion, at least three test pieces were used for each test. The results are reported as averages of the three or more tests performed.

2.3 The effect of process variables

To obtain good quality, reproducible chromate films on aluminium alloys the metal surfaces must be clean, uniform, and free of any gross oxide film. The time and temperature of the chromating stage must be controlled, as must subsequent washing and drying procedures. A set sequence was adopted and variations of the steps were investigated one by one. The procedure involved:

(a) degreasing by an approved method[7],

(b) pretreatment involving surface etching or deoxidizing,

(c) washing to remove pretreatment chemicals,

(d) immersing in the Marchand chromating bath,

(e) washing to remove chromating chemicals,

(f) drying.

After step (a) the test pieces were not touched by hand until after step (f), nor were they allowed to dry after step (b) until after step (e). Cold solvent degreasing was adequate for the reasonably clean test pieces used.

2.3.1 Pretreatments

Three pretreatments were used:

(a) etching[7] by Method 0 of Defence Standard 03-2,

(b) deoxidizing with a proprietary process A by immersion for 1-10 minutes at room temperature,

(c) deoxidizing with a proprietary process B by immersion for 2-10 minutes at room temperature.

The test pieces were suspended from glass hooks, degreased, and transferred to the pretreatment baths. After pretreatment, the metal surfaces were washed by suspending the test pieces for 5 minutes in a $2dm^3$ capacity bath through which mains water was passed at $3dm^3 \ min^{-1}$. The test pieces were allowed to drain (but not dry) and immersed for 3 minutes in a Marchand bath at 30°C. The make-up and working-in procedures for the bath are described in Appendix A. After treatment the test pieces were transferred to the wash bath for 1 minute, and then dried in a gentle stream of air at ambient temperature.

The coatings on BS L33 alloy pretreated by process (a) were patchy and easily detached by rubbing with a filter paper. Limiting the pretreatment (a) to 5 minutes, instead of the 20-30 minutes recommended, led to coatings which were uniform and adherent and this shorter pretreatment was adopted for BS L33 alloy.

The coatings were all of reasonably uniform colour and most of the coatings adhered well to the alloys: the exceptions were those applied to BS L16 and BS L33 test pieces after pretreatment (b). This process yielded chromate films with a blue, iridescent colouration, unlike the colour of coatings applied after pretreatments (a) and (c) which were iridescent and varied from pale straw to golden in colour. Exposure of test pieces to a continuous 5%

neutral salt fog revealed no differences in the corrosion resistance of the chromate coatings related to the pretreatment used.

The etch process (a), reduced to 5 minutes immersion for BS L33 alloy, was adopted as the standard pretreatment for the rest of the programme.

2.3.2 Time of immersion

The effect of immersion time on chromate films obtained on BS L16 test pieces was investigated, using a Marchand bath at 30°C. The overall process was modified so that the test pieces were dried and weighed after pretreatment, after chromating, and after stripping off the chromate film in 50% nitric acid. In this manner metal loss and chromate film mass were obtained. Also, the chromium content of the film was obtained by analysis of the nitric acid solution (see Appendix A). Immersion times in the Marchand bath of 20 seconds, and 1, 3, 9 and 27 minutes were used. The results, given in Table 1, indicate the possible errors in determining small metal losses (<100mg m^{-2}): metal loss measured after chromating for 1 minute was less than that measured after 20 seconds. Overall, the trends in the results are the expected ones, suggesting that as immersion time increases the rate of metal loss, and chromate film formation, decreases. Thus, 100nm of metal was lost after about 4 minutes immersion, 200nm after 20-25 minutes immersion; the chromate film thickness (estimated by assuming a density of 3g cm^{-3}) reached 100nm in 1-2 minutes, 300nm in about 6 minutes, and 400nm in about 20 minutes. The chromium content of the films was low (<15%) for immersion times of 20 seconds or 1 minute, and was highest (36%) after 3 minutes immersion. The films obtained after 20 seconds and 1 minute were almost colourless, the others golden yellow to deep golden coloured, and iridescent. Adhesion testing with a filter paper showed that some of the coating was removed from test pieces chromated for 3 minutes or longer, and the amount of transfer to the filter paper increased with immersion time. However, in no case was the film rubbed through and none of the coatings was powdery.

The above modified chromating technique could affect the efficiency of the process, and the tests were repeated without weighing the test pieces after the pretreatment, *i.e.*, metal loss was not determined. The determination of chromium content was also modified so that both total chromium and hexavalent chromium contents of the films were obtained (see Appendix A). The results, given in Table 2, indicate the same trends with regard to film thickness, but the chromium contents of the films were considerably increased after short immersion times. The films obtained after 3 minutes or 9 minutes immersion contained the largest proportion of chromium. The proportion of chromium in the hexavalent state determined for films obtained after 20 seconds immersion was very low (2.5%), but for the films obtained after longer immersion times the proportion was similar (14-18%).

Test pieces of BS L33, BS L71, and unclad BS L88 were chromated at 30°C for 1.5, 3, and 6 minutes. The coatings were all adherent, no material being removed by rubbing with filter paper. On BS L33 the films were a very pale straw colour and iridescent; on BS L71 they were iridescent, matt, and a pale straw colour; on BS L88 they were matt, iridescent, and gold coloured. The metal loss, film thickness, and chromium content of the films were determined as for BS L16 test pieces. The results are shown in Table 3 together with some of the results from chromating of BS L16 (from Table 1). It is apparent that the rate of metal loss of the three alloys is similar to that of BS L16. However, the resulting chromate films are thinner than those on BS L16. The chromium content of the films was not related to immersion time in any obvious way, varying between 13 and 28%. The results suggested that further investigation, probably using longer immersion times, was merited.

Test pieces of BS L71 were chromated at 30°C for 3, 9, and 27 minutes. The weight of the chromate films was obtained and both total chromium and hexavalent chromium were determined. The results are given in Table 4 together with comparative results from Table 2 on BS L16. It is again apparent that chromate films formed on BS L16 are thicker than those on BS L71, and this trend is greatest at the longest immersion time. The chromium contents of the films on BS L71 (31-36%) are nearly twice the values obtained in the previous tests (see Table 3) but are still less than the proportion of chromium found in filmed BS L16 test pieces. The amounts of hexavalent chromium found in the films on BS L71 were small (3-8% of total chromium) compared with those found in films on BS L16 (16-18%). Overall, increasing the immersion times from 3 minutes by factors of 3 and 9 led to increases in chromate film thickness and of available chromium by factors of 1.3 and 1.6 respectively. These gains in film thickness may not be worthwhile, especially as the films produced after 27 minutes immersion have a patchy appearance.

The two processes used in the determination of the chromate film thickness on both BS L16 and BS L71 test pieces led to different chromium contents in the films produced. When the test pieces were dried and weighed after pretreatment, chromating gave films containing significantly less chromium than those obtained by the standard procedure in which the test pieces were not allowed to dry prior to chromating.

2.3.3 Temperature of immersion

Test pieces of BS L16 were chromate filmed at 20, 30, 40, and 50°C for 3 minutes in the Marchand bath. All of the films were adherent; only a slight stain was observed on a filter paper after rubbing the test pieces. The colour varied from a straw colour to deep yellow for treatment temperatures from 20 to 50°C. All the films were iridescent. The films obtained at 50°C were 40% thicker than those obtained at 20°C, while the proportion of chromium in all of the coatings was similar. There appeared to be no significant advantage in operating at the higher temperatures, and the increased film thickness obtained at 50°C could equally well be achieved by increasing immersion time from 3 to 6 minutes at 30°C.

2.3.4 Washing procedures

After chromate filming at 30°C for 3 minutes, test pieces of BS L16 were washed in one of the following for 1 minute:

(a) cold mains water (temperature about 12°C)

(b) demineralized water (temperature about 20°C)

(c) hot mains water (temperature about 70°C)

(d) hot demineralized water (temperature about 70°C).

It is important that freshly chromated test pieces are gently lowered into a bath of the wash liquid since violent agitation or exposure to high speed jets of water can damage the fresh films. After washing, all of the coatings had similar adhesion properties and appearances. The coatings were dissolved in 50% nitric acid and found to be of similar mass, but those washed by procedures (b), (c) and (d) had slightly lower chromium content (up to 20% less) than those washed by procedure (a). However, the accuracy of the method (see Appendix A, section A.3) is such that the differences may not be significant. It is possible that washing the chromate films with demineralized or hot water may leach more chromium-containing salts from the films than would washing in cold mains water, and, as it was more convenient to use cold mains water, that medium was used throughout the remaining investigations.

2.3.5 Drying procedures

Chromated test pieces of BS L16 were washed in mains water for 1 minute and briefly in demineralized water before being dried in one of the following ways:

(a) in still laboratory air (temperature about 20°C)

(b) in a slow stream of laboratory air (temperature about 20°C)

(c) in a slow stream of warm air (temperature about 60°C)

(d) in a slow stream of hot air (temperature about 90°C).

The films dried by procedure (d) were insoluble in 50% nitric acid so that their thickness and chromium content were not determined. Those dried by processes (a) or (b) were of the same thickness and chromium content, within experimental error. The films dried in warm air (c), were only half the mass of those dried in cool air, (a) or (b), although the chromium content of films obtained after all three of the drying procedures was the same. These results suggest that the gel structure of the film is dehydrated by exposure to warm and hot air. Drying in hot air (*ca.* 90°C) may well lead to films which cannot provide leachable chromium to inhibit corrosion, and it would be sensible to avoid drying films at temperatures above 70°C. Films dried in static cool air had a streaky appearance whereas the use of a gentle stream of cool air (b) or of warm air (c) produced films with a uniform, pleasing appearance. The use of cool, circulating air was adopted for the rest of the programme.

2.4 Corrosion resistance

The test described in section 2.3 indicated that thin, poor quality films resulted from short immersion times (20 seconds or 1 minute) in the Marchand chromating solution, and patchy films resulted from long immersion (27 minutes). There appeared to be no advantage from chromate filming at temperatures above 30°C. Washing test pieces in hot or demineralized water after chromating may lead to loss of chromium from the film, and cold, mains water is suitable for washing. Drying chromate filmed test pieces in hot air can lead to insoluble films which may well be less efficient as anti-corrosion treatments. These results suggest that the optimum conditions may well be those described by Marchand: 3 minutes immersion at 30°C in the chromating solution followed by washing in mains water and drying at room temperature. These conditions are also more convenient than any in which elevated temperatures or long immersion times are involved.

A corrosion testing programme was performed to ensure that these chromate filming conditions result in films with adequate corrosion resistance, and to see whether changes in immersion time and temperature of the chromating process lead to films with significantly different corrosion resistance. In the laboratory the ARE salt droplet test[5] and salt fog test[4] were used, while natural environment testing was done at both rural and marine sites with all of the test pieces being exposed within one month from mid-October to mid-November. The tests were described in section 2.2.

Initially the corrosion resistance of BS L16 test pieces chromate filmed by immersion for 1.5, 3, and 6 minutes at 30°C, and 3 minutes at 20°C and at 40°C was compared with unfilmed and anodized test pieces. In both marine and rural environment tests some corrosion occurred with all of the test pieces within the 12 months' duration of the tests. However, it was not possible to detect accurately the onset of corrosion. In general the uncoated materials showed the first signs of corrosion after 1-2 months and the chromated test pieces after 3-8 months, with no detectable differences between test pieces chromated under different conditions. At the end of the year's test, it was not possible to relate the extent of corrosion to the chromate filming conditions used, all of the test pieces showing light corrosion. The unprotected test pieces were more badly corroded and the anodized ones showed breakdown of the coating in one or two places only. Laboratory corrosion tests were no more productive in differentiating between the variously chromated test pieces. The salt droplet test failed to corrode any chromated or anodized test piece and corrosion of unprotected BS L16 sheet alloy was only evident at the end of the test after washing and drying the test pieces. Continuous 5% neutral salt fog caused corrosion of all of the test pieces but it was not possible to detect the onset of corrosion with any accuracy. At the end of 30 days exposure to salt fog the test pieces were washed, dried, and assessed for the extent of corrosion. The unprotected test pieces were moderately corroded. All of the chromated test pieces showed similar, very light corrosion, and the anodized test pieces showed less than ten breaks in the surface film. The appearance of typical BS L16 test pieces after corrosion testing is illustrated in Fig.1.

Corrosion testing of BS L33, chromate filmed for 3 minutes at 20°C, 1.5 minutes at 30°C, and 3 minutes at 30°C, in both marine and rural environments failed to show any differences in corrosion resistance of the various coatings: all of the test pieces showed light corrosion on machined surfaces but no corrosion on the as-cast surfaces. Unchromated test pieces showed only slightly more corrosion than chromated ones, while anodized material did not corrode. The salt droplet test did not cause corrosion of any BS L33 material. In contrast, continuous 5% neutral salt fog caused corrosion of all BS L33 test pieces; the onset of corrosion of unprotected test pieces occurred within 24 hours, of chromated test pieces between 5 and 7 days, and of anodized test pieces between 10 and 15 days. There were no detectable differences in the corrosion resistance of the variously chromated test pieces. The appearance of typical test pieces of BS L33 after corrosion testing is illustrated in Fig.2.

Both of the laboratory corrosion tests demonstrated the differences in corrosion resistance of unprotected, chromated, and anodized test pieces of BS L71 and unclad BS L88 (see Table 5). The tests also indicated that materials chromated at 30°C for 3 minutes were slightly more resistant to corrosion than those chromated at 20°C for 3 minutes, or at 30°C for 1.5 minutes. Typical corroded test pieces are shown in Figs.3 and 4. In contrast, natural environmental testing showed little or no difference in the corrosion resistance of chromated and unprotected test pieces of BS L71: corrosion was noted at the first inspection of the test pieces, 1 week after exposure, and after 4-5 weeks all of the test pieces were quite badly corroded. Anodized test pieces were more resistant: in a marine environment corrosion commenced within 2 weeks of exposure, and in a rural environment within 26 weeks. Natural environment tests on BS L88 alloy were difficult to interpret because at the end of the test period the bottom surfaces of both chromated and anodized test pieces were found to be more badly corroded than the upper surfaces. This could invalidate the observed onset of corrosion because only the upper surfaces could be carefully examined at those stages. However, there were differences in the corrosion resistance of chromated and unprotected material and, in the marine exposure trials, there were apparent differences in corrosion resistance of test pieces chromated under different conditions. However, these differences indicated superior corrosion resistance for test pieces chromated at $20^{\circ}C$ compared with those chromated at $30^{\circ}C$, whereas the reverse would be expected. The corrosion which occurred on the BS L88 test pieces was very difficult to detect: very small pits formed and no massive corrosion product appeared on the test piece as happened with BS L71 alloy. The results of natural environment corrosion testing of BS L71 and unclad BS L88 are given in Table 6 and typical corroded test pieces are illustrated in Figs.5 and 6.

All of the corrosion tests indicated that chromated BS L71 is the least corrosion resistant of all of the chromated alloys. Also the onset of corrosion was easy to detect because initial breakdown of the chromate film was accompanied by the appearance of relatively large areas of white corrosion product (see Figs.3, 5 and 7). Exposure to continuous 5% neutral salt fog gave reasonably rapid results: uncoated alloy corroded within 2 hours, chromated material between 5 and 7 days, and anodized material after 10 days exposure. The main criticism of the test is that initial corrosion of anodized and chromated test pieces is not greatly different. However, if the amount of corrosion is also taken into account, it is clear that the anodic films are superior to chromate films: after 7-10 days the chromated test pieces are badly corroded, whereas anodized material shows only light to moderate corrosion after 30 days.

The natural environmental tests were disappointing in that they did not discriminate between chromate coatings of different corrosion resistance and, in the case of BS L71, between chromated and unchromated material. It was difficult to understand the large differences in the rural environment tests in the time to first corrosion of chromate filmed BS L71 and BS L88 test pieces. The former corroded within a week but the latter survived for about 6 months. Two factors are worth noting. Corrosion was difficult to detect on the BS L88 on which material the lower surfaces were more badly corroded at the end of 1 year, and the BS L88 test pieces were exposed 3 weeks after the BS L71. The danger in not exposing test pieces at the same time was emphasized by subsequent marine and rural exposure testing of Marchand chromated test pieces of BS L71 and material chromate filmed by two proprietary processes (see section 3). These tests were started at the same time, mid-February; no corrosion was observed after 2 weeks' exposure and all the chromated test pieces had started to corrode after 3 weeks, contrasting with a time to first corrosion of less than 1 week for the test pieces exposed in mid-October.

2.5 Assessment of bath life

The solutions used for chromic acid based conversion coating processes change with use; chromic acid is consumed, the pH of the solution rises, and the quality of the chromate coatings deteriorates. It is important to establish the parameters which control the useful life of the solutions. In the case of the Marchand bath, the corrosion resistance of chromated BS L71 test pieces was used to identify solutions which did not give acceptable chromate films. With use chromic acid is consumed, and the dichromate ion concentration and pH of the Marchand bath increase.

An initial evaluation was made of the compositional limits which would give acceptable chromate films by making baths with various chromic acid and sodium dichromate concentrations. The ranges covered were 3.5-1.8g dm^{-3} chromium trioxide and 3.5-5.5g dm^{-3} sodium dichromate, with a sodium fluoride concentration of 0.8g dm^{-3}. Chromate films were applied to BS L71 test pieces by the normal procedure, using an immersion time of 3 minutes at 30°C. The filmed test pieces were exposed to continuous 5% neutral salt fog until first corrosion was noted. All test pieces chromated in baths containing more than 2.3g dm^{-3} of chromium trioxide and less than 5.0g dm^{-3} of sodium dichromate survived for at least 5 days before corrosion started. Test pieces chromated in a bath containing 1.8g dm^{-3} of chromium trioxide and 5.5g dm^{-3} of sodium dichromate showed corrosive breakdown of the films within 2 days. The pH of the various baths was not greatly different: the normal concentration Marchand bath had pH 1.9 when freshly prepared while the bath giving poor quality films (1.8g dm^{-3} CrO_3 and 5.5g dm^{-3} $Na_2Cr_2O_7.2H_2O$) had pH 2.6.

A Marchand bath of normal concentration was used for chromating BS L16 and BS L71 test pieces until 80 test pieces had been filmed (3 minutes immersion at 30°C). BS L71 chromated in this bath did not show any corrosion for 5 days when exposed to continuous 5% neutral salt fog. At this stage several test pieces were chromate filmed for various times and at various temperatures, and their corrosion resistance assessed. The results are given in Table 7. Test pieces filmed at 20°C for 3 minutes corroded before 3 days' exposure to the salt fog test, those filmed at 30°C for 3 or 9 minutes corroded after 4 days, and those filmed at 30°C for 27 minutes lasted less than 5 days in the corrosion test. Typical test pieces are shown in Fig.7. The Marchand bath was analysed (using a method described in Appendix A) and found to contain 2.2g dm^{-3} of chromium trioxide, the equivalent of 6.5g dm^{-3} sodium dichromate, and 0.8g dm^{-3} of sodium fluoride; the pH was 2.2.

It is noteworthy that there was no marked difference in appearance between chromate filmed test pieces that performed well in the salt fog test and those that corroded in under 5 days. Consequently it is prudent to monitor the chemical composition of the Marchand bath, or to ensure that the area of alloy surface filmed is related to the volume of the bath solution. A regular check on the pH will give some indication on the condition of the bath, but the small range of values (pH 1.9-2.2) over which the bath is usable makes this method of limited use. Allowing a reasonable safety margin the chromium trioxide concentration should be over 2.5g dm^{-3}, the sodium dichromate concentration less than 4.8g dm^{-3}, and not more than 0.4m^2 of alloy should be filmed per dm^3 capacity of the bath. Sodium fluoride concentration does not seem to vary with use very greatly but it may be prudent to maintain the concentration within 15% of the original value.

2.6 Alternative chromate filming techniques

An important use of chromate conversion coatings is in the repair of protective schemes: damaged painted surfaces are repaired (after removal of loose paint and any corrosion product) by brush, swab or spray application of a chromating solution followed by an approved paint scheme; anodic films are repaired (or 'freshened') by similar local application of chromating solutions. The use of Marchand solutions in such situations was assessed to see whether acceptable adhesion, appearance, and corrosion resistance were obtained.

The central areas of test pieces (100 × 50mm) previously chromated by immersion (3 minutes at 30°C) were abraded with a Scotchbrite pad to within 10mm of the edges. These surfaces were then treated in one of four ways with Marchand solution at ambient temperature (*ca.* 20°C):

(a) the solution was applied by firmly swabbing the vertical surface with a cotton wool pad, commencing at the bottom. Swabbing was repeated every 20 seconds over periods of 3 or 9 minutes,

(b) a similar swab application but to a horizontal surface,

(c) spray application onto a vertical surface using a DeVilbiss type MPS spray gun (No.2 fluid tip and air cap). Spraying was repeated every 20 seconds over periods of 3 or 9 minutes,

(d) a similar spray application but to a horizontal surface.

After the application of Marchand solution the test pieces were washed and dried as before (sections 2.3.4, 2.3.5).

Initially, tests were done on BS L16, BS L71, and unclad BS L88 using the normal concentration Marchand solution (chromium trioxide 3.5g dm^{-3}, sodium dichromate 3.5g dm^{-3}, and sodium fluoride 0.8g dm^{-3}), but the corrosion resistance of the spray-applied chromate films was poor. Further tests were done on BS L71 alone using a more concentrated solution: chromium trioxide 14g dm^{-3}, sodium dichromate 14g dm^{-3}, and sodium fluoride 3.2g dm^{-3}. The corrosion resistance of these spray-applied chromate films was still inferior to those obtained by immersion. In contrast, all of the swab-applied coatings provided good corrosion resistance. Those applied to BS L16 behaved in a similar manner to chromate films obtained by immersion: corrosion of the test pieces was only observed towards the end of the salt fog test (between 28 and 30 days). Those applied to BS L71 and to unclad BS L88 were superior to the immersion coatings, judged on the time to first corrosion. The results are given in Table 8.

These results suggest that swab application at 20°C for 3 minutes is adequate to form chromate films with good corrosion resistance. Either a normal concentration or a more concentrated Marchand solution may be used; both give adherent, golden-coloured, iridescent films. Application by spray leads to poor quality films.

3 PROPRIETARY CHROMATE CONVERSION COATINGS FOR ALUMINIUM

There are several commercial processes which employ immersion in a chromic acid based bath for chromate filming of aluminium and its alloys. Two widely used processes, approved to DTD 900, which give rise to golden-coloured, iridescent films were compared with the Marchand process. They will be referred to as process X and process Y.

Chromate films were applied according to the manufacturer's instructions to test pieces of BS L16 and BS L71. For process X this involved initial degreasing before treatment with deoxidizer B (see section 2.3.1), washing, and immersion for 3 minutes at 20°C in the chromating solution. For process Y the test pieces were prepared as for the Marchand process and chromated by immersion at 30°C for 3 minutes. The chromated alloys were washed and dried as for the Marchand process. The metal loss during chromating, the chromate film thickness and chromium content were determined as for the Marchand chromate films (see section 2.3.2). The results are given in Table 9, together with results using the Marchand process. Metal loss of BS L16 and BS L71 is greatest in process Y (170 and 150nm respectively) and least in process X (72 and 33nm); the Marchand process leads to intermediate values (82 and 120nm). The resulting chromate films are quite thick from both process X (970 and 490mg m^{-2}) and process Y (1160 and 620mg m^{-2}) compared with those from the Marchand process (420-440 and 280-340mg m^{-2}) after 3 minutes immersion at 30°C. By increasing the immersion time to 27 minutes at 30°C the Marchand process produces films of similar thickness to the proprietary processes (960 and 460mg m^{-2}). The chromium content of the films from both processes X and Y is reasonably constant at 26-29 wt.% whereas higher but more variable chromium contents were measured in the Marchand process (16 and 32 wt.% on BS L71, 36 and 43 wt.% on BS L16).

Corrosion resistance of the chromate films produced on BS L71 alloy by the two proprietary processes and by the Marchand process were compared by exposure to both rural and marine environments. Test pieces filmed for 3, 9, and 27 minutes by the Marchand process, and uncoated test pieces were exposed together with test pieces filmed by processes X and Y, exposure commencing in mid-February. After 1 week the unprotected test pieces had started to corrode; after 2 weeks all of the chromate filmed test pieces were uncorroded although some loss of colour was noted: after 3 weeks all of the chromate filmed test pieces had started to corrode, those treated for 3 and 9 minutes at 30°C by the Marchand process and by process X had lost most of their yellow colouration, and those treated for 27 minutes at 30°C by the Marchand process and by process Y were still yellow. The amount of corrosion present was least on the test pieces which had retained most of their yellow colouration.

Two laboratory corrosion tests were used. As well as the salt fog test, alternate immersion into 3.5% neutral salt solution was used to see whether a cycle involving immersion for 10 minutes followed by drying for 50 minutes would cause more severe corrosion of any one of the three chromate film types. Chromate filmed test pieces were scratched through to the metal on one side to form a grid of 100 interconnected squares (2 × 2mm): it was hoped that test results on the damaged surfaces would differentiate between coatings on the basis of availability of leachable corrosion inhibitors in the films. Half of the test pieces were kept in the laboratory at ambient temperature for 12 days before corrosion testing, and the other half were tested within 24 hours of filming. Any adverse effects due to aging of the coatings should be detected in this way. The results based on the time to first corrosion are given in Table 10, and the appearance of typical test pieces several days after the first corrosion was noted is illustrated in Fig.8.

The corrosion resistance of the different chromate films was very similar. In the salt fog test, damaged fresh films from process X showed better corrosion resistance than the other films. In all of the other tests, based on time to first corrosion, the results did not differentiate between the three types of chromate film. However, on further exposure to the test environments the Marchand-chromated test pieces tended to show more corrosion than the two proprietary process films. This was more marked with the alternate immersion test (see Fig.8).

Overall, there were no major differences, judged on the time to first corrosion, in the corrosion resistance of the three chromate films despite the marked differences in the thickness of the coatings.

4 PAINT ADHESION

The major use of chromate filming of aluminium alloys in the aircraft industry is as a pretreatment to provide a uniform, stable metal surface with good adhesion to subsequently applied paint schemes. The Marchand chromate filming process was evaluated by painting test pieces (100 × 50mm) of BS L16, BS L33, BS L71, and unclad BS L88, which had been chromate filmed using optimum conditions (3 minutes at 30°C), for twice the optimum time (6 minutes at 30°C), and at 10°C above the optimum temperature (3 minutes at 40°C). These chromating treatments were used to establish whether thicker than optimum films would lead to (a) poorer paint adhesion or (b) better corrosion resistance. The paint scheme was to DTD 5555A: a chromate-pigmented primer was applied followed by a glossy white epoxy top-coat. The paint was applied within 24 hours of chromate filming, and was allowed to cure for 7 days at room temperature.

Two lattice patterns were cut on one face of the painted test pieces, penetrating the paint scheme into the metal substrate, according to[8] BS 3900 part E6. Each pattern was a cross-cut area containing 100 squares (2 × 2mm). A typical test piece after preparation is shown in Fig.9 and details of the technique are given in Appendix B. The cross-cut areas were examined and classified according to the scale suggested in BS 3900 part E6 (classification 0 indicating completely smooth cuts with no material detached from the squares, classification 1 indicating less than 5% of the paint lost within the cross-cut areas, and classification 2 indicating loss of 5 to 15% of the paint within the cross-cut areas). One of the cross-cut areas was then subjected to the adhesion test given[5] in Appendix C of BS 1391, involving covering the area with a strip of adhesive cellulose tape and then removing it with a specific force: details are given in Appendix B. All of the cross-cut areas were to classification 0 and no paint loss occurred during the tape test.

The test pieces were exposed to continuous 5% neutral salt fog for 30 days before being washed in tap water and dried for 24 hours at room temperature. Examination showed some paint blistering on one BS L16, on two BS L33, and two BS L71 test pieces. Nine test pieces of each alloy had been used. The tape test was applied to the second cross-cut area and loss of paint was observed from half of the test pieces. The results are summarized in Table 11.

Comparative tests were done on painted BS L16 and BS L71 test pieces, chromate filmed with the two proprietary processes X and Y. No loss of paint occurred in the tape test before exposure to continuous 5% neutral salt fog, but after 30 days' exposure, 9 of the 24 test pieces showed signs of paint blistering in the cross-cut areas, and 11 of the test pieces showed paint loss after the tape test. The results are summarized in Table 12.

Figs.10 and 11 show examples of painted BS L71 test pieces which showed (a) no loss of paint, and (b) the greatest loss of paint, after exposure to the salt fog environment and the tape test. The test piece in Figs.10(a) and 11(a) was chromate filmed by the Marchand process at 40°C, and that in Figs.10(b) and 11(b) by process X.

In summary, the tests showed that paint adhesion to all of the chromate films was excellent, and therefore there was no advantage in using the proprietary processes. After exposure to continuous salt fog, paint adhesion to BS L16 test pieces was better on proprietary chromate filmed test pieces, but on BS L71 was slightly better on the Marchand-chromate filmed alloy. The paint adhesion to the Marchand-filmed BS L16 test pieces was surprisingly poor, being no better, after exposure to a salt fog, than on BS L33 test pieces, and inferior to that on unclad BS L88 test pieces.

5 DISCUSSION

Chromate filming of aluminium, cadmium, and zinc surfaces improves their corrosion resistance, especially in humid environments, and this effect is utilized as a relatively inexpensive method of protecting these metals. A Defence Specification[9] describes an approved process for chromate filming of cadmium and zinc, especially electroplated cadmium and zinc, and zinc-base alloy die-castings. For aluminium and its alloys several processes are approved in the DTD 900 series but no Defence Standard, giving a performance requirement, has been issued. Before such a document could be drafted it was necessary to understand the factors affecting the performance of chromate films on aluminium and to this end the process described by Marchand[1] was used.

The investigations described in section 2.3 showed that the Marchand process of chromate filming, by immersion of aluminium alloy for 3 minutes at 30°C in the chromic acid/dichromate/fluoride bath, was not sensitive to pretreatment, washing, or drying variables, except that drying above 70°C resulted in insoluble films which might well be less effective corrosion inhibitors. Varying the time and temperature of immersion in the chromating bath did influence the thickness of chromate films obtained. Comparison with chromate films from two proprietary processes showed that 27 minutes immersion at 30°C in the Marchand bath was required to obtain films of similar thickness, while immersion for 3 minutes gave films only half as thick. Changing the treatment temperature from 20 to 50°C resulted in an increase of only 40% in film thickness. Treatments for much less than 3 minutes naturally led to thinner films and such short times are probably impracticable if even chromate filming of complex components is required. There were marked differences in the amount of metal loss during the chromate filming process: one proprietary process caused far less metal loss than did the Marchand or the other proprietary process.

Despite these variations in chromate film thickness and of metal loss, there were no detectable differences in the corrosion resistance conferred by the three processes. In comparative natural environment tests, using chromate-filmed BS L71 test pieces, the time to first corrosion was the same for test pieces chromated by either of the two proprietary processes or by the Marchand process. And test pieces filmed for 3, 9 and 27 minutes at 30°C by the Marchand process started to corrode after the same period of exposure. Laboratory corrosion tests showed little or no difference in the time to first corrosion of the variously chromate filmed test pieces, although there were indications that further deterioration was more rapid with Marchand-chromated alloy.

The corrosion resistance of BS L16, BS L33, and unclad BS L88 alloys chromated by the Marchand process was investigated. In all of the tests used chromated BS L71 was more susceptible to corrosion than the other alloys. Consequently, BS L71 was used for most of the comparative testing with proprietary chromate-filming processes, and it or similar Al-Cu alloys should be adopted in any performance or quality control tests for chromate filming of aluminium alloys. The continuous 5% neutral salt fog test was the easiest test to apply, and it was the most discriminating test with respect to the corrosion resistance quality of chromate films. For these reasons it should be used for performance and quality control tests for chromate filming treatments. Under carefully controlled laboratory conditions, the Marchand process gives chromate films on BS L71 which, when applied at 20°C for 3 minutes, show no corrosion in the salt fog test for 5 days, and, when applied at 30°C for 3 minutes, for 7 days. Applications under less ideal conditions should give chromate films by immersion at 30°C for 3-6 minutes which survive at least 4 days in the salt fog test without corrosion. Operations at 20°C may require extended treatments (say 9 minutes) and operating at 40°C should not require more than 3 minutes to produce adequate chromate films.

Swab-application of Marchand solutions produced good chromate films. Solutions of normal concentration and a four-fold increase in concentration of the chemicals were used, the latter giving slightly better corrosion resistance. Allowing for the difficulties that may be faced in applications to complex or large components it would probably be safer to use the more concentrated solution. Swabbing for 2-4 minutes at ambient temperatures around 20°C should be quite adequate to give corrosion-resistant films. Application by spray was not very successful, even using the concentrated solution, and the resulting films had corrosion resistance significantly poorer than immersion-applied films.

The life of the Marchand bath was disappointingly short: about 0.4m^2 of alloy surface could be chromated by immersion in a 1dm^3 capacity bath before the corrosion resistance of the resulting films was dramatically reduced. It is probable that the life of the bath can be extended by additions of an acid (such as nitric acid) to maintain the pH at the original value of a freshly prepared bath. The resultant lowering of pH would lead to the conversion of dichromate ion to chromic acid:

$$Cr_2O_7^{--} + 2H^+ + H_2O \rightarrow 2H_2CrO_4$$

i.e., it would reverse the change occurring as the bath was being used for chromating. However, the effect of introducing another variable into the chromating solution would require an assessment of performance of such baths after addition of various amounts of acid. This was not possible in the time-scale available for the basic evaluation of the process. The change of pH and composition of the Marchand bath during use must be monitored to avoid sub-standard chromate filming, especially as the appearance of chromate films with poor corrosion resistance obtained from a depleted bath are very little different from films with good corrosion resistance obtained from a fresh bath. Analysis by a simple potentiometric titration proved to be a very satisfactory method whereas measurement of pH is probably too insensitive.

Good paint adhesion to chromate films is probably more important than the corrosion resistance of the chromate films, for it is as a surface pretreatment prior to painting that chromate filming is mainly used in the aircraft industry. The painting takes place as soon as is practicable after chromating, invariably within 24 hours. In the evaluation of adhesion to the three types of chromate films a British Standard test method[8] was used in which the paint scheme (to DTD 5555) was cut through to the metal to form a cross-cut area containing 100 squares, 2 × 2mm. In no case was there evidence of any but excellent adhesion to the chromate films. And attempts to detach paint from the cross-cut areas, by means of adhesive tape pressed onto the paint surface and then removed with a sudden jerk[5], did not result in loss of paint due to failure of the paint to chromate film bond, or chromate film to metal bond. The adhesion of damaged paint films after exposure to a corrosive environment was assessed, and all combinations of paint scheme and chromate films performed in a similar manner. Test pieces of BS L71 were most susceptible to loss of paint after exposure to salt fog and this, or a similar Al-Cu alloy, should be used for quality control or performance tests for chromate filming processes. In this programme, of 21 chromated BS L71 test pieces only two showed more than 5%, and less than 15%, loss of paint after exposure to the salt fog test and application of the adhesive tape test. This minimum standard of performance should be required of any chromate filming process.

6 CONCLUSIONS

(1) The Marchand process produces iridescent, straw to golden-coloured chromate films on aluminium and its alloys. The corrosion resistance of these films is similar to those obtained by two proprietary processes.

(2) Marchand process chromate filming can be conveniently performed by immersion of the clean, etched metal in an aqueous solution of chromium trioxide (3.5g dm^{-3}), sodium dichromate (3.5g dm^{-3}), and sodium fluoride (0.8g dm^{-3}) for 3 minutes at 30°C; adjustments of the conditions between 3 and 9 minutes and 20 and 40°C should have little effect on film properties if the longer times are only used at the lower temperatures.

(3) It is essential that, in use, the Marchand solution is monitored by *chemical analysis*, or the surface area of metal chromated in a given volume of solution is restricted to ensure that the concentrations of chemicals in the solution do not change so that the chromium trioxide content falls below 2.5g dm^{-3} and sodium dichromate rises aboves 4.8g dm^{-3}. It may also be useful to check that the sodium fluoride concentration does not fall below 0.7g dm^{-3}.

(4) Chromate filming can also be achieved by swabbing the metal with solutions employed for immersion, or with more concentrated solutions. Swabbing with a solution of chromium trioxide (14g dm^{-3}), sodium dichromate (14g dm^{-3}), and sodium fluoride (3.2g dm^{-3}) for 2 to 4 minutes at 20°C gave good quality chromate films.

(5) Corrosion resistance of the chromate films is best assessed by exposure to a continuous 5% neutral salt fog. Other corrosive environments investigated did not discriminate as readily between chromate films of different corrosion resistance.

(6) Chromate filmed BS L71 alloy was the most susceptible to corrosion of those investigated. This alloy, or related materials (BS L150, *etc.*), should therefore be used to evaluate the corrosion resistance conferred by chromate filming processes.

(7) No differences were detected in the paint adhesion to chromate films produced by the Marchand process or by two proprietary processes

(8) Paint adhesion can be assessed using a chromate-containing epoxy primer applied within 24 hours of chromate filming followed by an approved top-coat, and using two British Standard test methods involving a cross-cut test and an adhesive tape test; assessments can be made before and after exposure to continuous 5% neutral salt fog.

Acknowledgments

The authors thank Mr. A.R.G. Brown who planned this programme, and Mr. I.H. Parrott who performed the initial experimental work, and Central Dockyard Laboratory for the use of the marine environment corrosion test site at the Exposure Trials Station, Eastney.

Appendix A

DETAILED PROCEDURES FOR USING AND ASSESSING MARCHAND CHROMATE FILMING BATHS

(see sections 2.3.1, 2.3.2 and 2.5)

A.1 Initial operation of a Marchand bath

The solution used contains fluoride ion and oxidizing agents at pH 1.9. Containers resistant to these materials must be used, and the most useful material for use as laboratory-scale baths is polyethylene (glass is attacked by acidic fluoride ion solutions). The solution of chromium trioxide (3.5g), sodium dichromate as the dihydrate (3.5g), and sodium fluoride (0.8g) in distilled water (to $1 dm^3$) does not initially form good quality chromate films on aluminium, and it is necessary to treat between 2.5 and $5 dm^2$ of BS L16 for 3 minutes at $30^\circ C$ in the bath before normal, golden-coloured, iridescent films are obtained.

A.2 Determination of metal loss and chromate film weight on freshly chromated test pieces

To determine metal loss during chromate filming the overall process was modified in that the test piece was thoroughly dried after pretreatment and washing. While dry the test piece (mass between 10 and 20g) was weighed to ±0.1mg (weight = W_1). It was then immersed in the chromate bath, washed, and dried by the normal procedure before being weighed again (W_2). The chromate film was then removed by immersing in 25% nitric acid (40ml) at $20-40^\circ C$. Freshly deposited films dissolved within 5 minutes. The test piece was washed and dried before weighing again (W_3). Metal loss during the filming process was (W_1-W_3), and the chromate film mass was (W_2-W_3). The accuracy of the values for weight loss and film thickness could only be ±0.2mg which represents ±20% on values of $200mg\ m^{-2}$, typical of values obtained for weight loss on immersion for 3 minutes at $30^\circ C$, and for films obtained after 1-1.5 minutes at $30^\circ C$.

A.3 Determination of chromium content of the chromate films

(a) Total chromium was determined by atomic absorption spectrophotometry. The nitric acid solutions (from A.2) of the chromate film were diluted to 100ml and analysed to 1ppm. Thus the analysis of films formed by immersion of BS L71 for 3 minutes at $30^\circ C$, containing $55mg\ m^{-2}$ chromium, would only be accurate to ±15%.

(b) Hexavalent chromium was determined using the nitric acid solutions (from A.2) of the chromate films. The solution was made alkaline to litmus by addition of dilute sodium hydroxide, the solution being cooled during the addition. Trivalent chromium was then present as chromite ion and hexavalent chromium as chromate. The volume of the solution was measured to ±1% and an aliquot examined by ultra-violet spectrophotometry, the absorbance at 373nm (specific for chromate) being determined. From measurements of the absorbance of standard sodium chromate solutions the hexavalent chromium content of the original solution was obtained. The original, alkaline solution, together with the aliquot examined, was boiled for a few minutes with hydrogen peroxide (*ca.* 1cm^3, 20vol.) to oxidize chromite to chromate. The solution was cooled and its volume measured before an aliquot was examined to determine the hexavalent chromium content - equal to the total chromium content of the original nitric acid solution.

The accuracy of the determination of hexavalent chromium was limited by its tendency to reduce to the trivalent state in nitric acid. Hence, the values of hexavalent chromium given in Tables 2 and 4 should be treated as *minimum* values. The overall limit of accuracy of this method (*i.e.*, for the determination of total chromium) is ±0.05ppm, which represents ±3% on the values of total chromium obtained in chromate films on BS L16 after 20 seconds immersion at 30°C in the Marchand bath.

A.4 Analysis of Marchand baths

The chromic acid and dichromate ion concentrations were readily obtained by potentiometric titrations with alkali, to end-points at pH 4.4 for the conversion:-

$$2H_2CrO_4 + 2OH^- \rightarrow Cr_2O_7^{--} + 3H_2O \ ,$$

and at pH 8.2 for the conversion:-

$$Cr_2O_7^{--} + 2OH^- \rightarrow 2CrO_4^{--} + H_2O \ .$$

The following procedure was used:

A 25cm^3 aliquot was titrated with 0.1M NaOH to pH 4.4 (volume of titrant = V_1 cm^3), and then to pH 8.2 (total volume of titrant = V_2 cm^3).

The concentration of chromium trioxide present in the bath = $0.4V_1$ g dm^{-3}, and the concentration of dichromate (expressed as $Na_2Cr_2O_7.2H_2O$) = $0.596(V_2 - 2V_1)$ g dm^{-3}.

To obtain the fluoride ion concentration, $30cm^3$ of 30 wt.% sodium citrate was added to the solution (titrated with alkali to pH 8.2), and then diluted to $100cm^3$. A selective fluoride ion electrode is immersed in this solution and the millivoltmeter reading persisting for 1 minute was recorded. Solutions containing chromium trioxide (3.5g dm^{-3}), sodium dichromate (3.5g dm^{-3}), and various concentrations of sodium fluoride, were titrated to pH 8.2 with alkali and then treated with sodium citrate as above. The millivoltmeter recordings were plotted against sodium fluoride concentration and, using the millivoltmeter value recorded for the unknown solution, the concentration of sodium fluoride was obtained from the graph.

Appendix B

THE PREPARATION OF PAINTED TEST PIECES

(see section 4)

Test pieces (100 × 50mm) were chromate filmed and then over-coated with a chromate-pigmented epoxy primer according to the specification DTD 5555, within 24 hours of chromate filming. The primer and subsequently applied glossy white epoxy top-coat (to DTD 5555) were spray-applied and allowed to cure at room temperature for 7 days. Two cross-cut patterns were applied on one face of each test piece (see Fig.9), using a 2mm spacing. The guide described in BS 3900, part E6 was used, but for cutting the patterns a steel knife was used, ground to a 30^{o} cutting edge, 50μm wide. The tool, which was re-sharpened when the edge became 80μm wide, was of the same geometry at the cutting edge as the circular tool described in BS 3900 part E6, but it was found to be more convenient in use. The cuts were made at a cutting rate of 20 to 50mm s^{-1} with sufficient pressure to penetrate into the metal substrate. One operator made all of the cross-cut patterns to ensure constant penetration into the metal substrate. The depth of the cuts was found to be 75 ±10μm below the paint surface, and 25 ±10μm below the metal surface.

Clear cellulose adhesive tape, 25mm wide, was used for the tape-test described in BS 1391 Appendix C. A strip of tape about 125mm long was used, and about 50mm of one end was pressed firmly over one cross-cut area, ensuring complete contact and exclusion of air bubbles. The test piece was supported horizontally in such a way that the taped area faced downwards with no obstruction below it. The free end of the tape was attached *via* a suitable connection to a mass of 907g. The test was arranged so that when the 907g mass was released, it fell through 30cm before removing the tape. The adhesive tape so removed was mounted onto a transparent sheet of polyethylene. In this way permanent records were obtained of the amount and pattern of paint removed. The test piece and tape were both examined; the former showing any adhesive failure at the metal surface and the latter cohesive and adhesive failure in the paint film. The amount of paint lost by adhesive failure was estimated for the purposes of these tests, and to give the results in Tables 11 and 12.

Table 1

EFFECT OF IMMERSION TIME AT 30°C IN THE MARCHAND BATH ON THE THICKNESS AND COMPOSITION OF CHROMATE FILMS ON BS L16, AND METAL LOSS DURING CHROMATE FILMING

Immersion time	Metal loss during filming		Chromate film thickness		Chromium content of film	
	mg m^{-2}	nm	mg m^{-2}	nm*	Weight of chromium mg m^{-2}	Weight % of chromium
20 seconds	80	30	60	20	8	13
1 minute	60	22	260	87	26	10
3 minutes	220	82	420	140	150	36
9 minutes	400	150	1080	360	200	19
27 minutes	620	230	1280	430	400	31

* Assuming a density of 3.0g cm^{-3}

Table 2

EFFECT OF IMMERSION TIME AT 30°C IN THE MARCHAND BATH ON THE THICKNESS AND COMPOSITION OF CHROMATE FILMS ON BS L16

Immersion time	Chromate film thickness		Chromium content of the film			% of chromium present as Cr^{6+}
			Weight of chromium, mg m^{-2}		Weight % of total chromium	
	mg m^{-2}	nm*	As Cr^{6+}	Total chromium		
20 seconds	130	43	0.8	32	25	2.5
1 minute	290	97	14	100	34	14
3 minutes	440	150	29	190	43	16
9 minutes	570	190	46	250	43	18
27 minutes	960	320	62	360	37	17

* Assuming a density of 3.0g cm^{-3}

Table 3

EFFECT OF IMMERSION TIME IN THE MARCHAND BATH ON THE THICKNESS AND COMPOSITION OF CHROMATE FILMS ON THREE ALUMINIUM ALLOYS, AND METAL LOSS DURING FILMING

Material	Immersion time	Metal loss during filming		Chromate film thickness		Chromium content of the film	
		$mg\ m^{-2}$	nm	$mg\ m^{-2}$	nm*	Weight of chromium $mg\ m^{-2}$	Weight % of chromium
BS L16	1 minute	60	22	260	87	26	10
BS L33	1.5 minutes	100	38	240	80	68	28
BS L71		180	64	200	67	25	13
BS L88**		180	64	220	73	37	17
BS L16	3 minutes	220	82	420	140	150	36
BS L33		240	91	280	93	60	21
BS L71		320	120	340	110	55	16
BS L88**		200	71	240	80	49	21
BS L33	6 minutes	420	160	460	150	65	14
BS L71		360	130	360	120	83	23
BS L88**		220	79	200	66	54	27
BS L16	9 minutes	400	150	1080	360	200	19

* Assuming a density of $3.0g\ cm^{-3}$
** Cladding removed

Table 4

EFFECT OF IMMERSION TIME AT 30°C IN THE MARCHAND BATH ON THE THICKNESS AND COMPOSITION OF CHROMATE FILMS ON BS L16 AND BS L71

Material	Immersion time	Chromate film thickness		Chromium content of the film			% of chromium present as Cr^{6+}
				Weight of chromium, mg m^{-2}		Weight % of total chromium	
		mg m^{-2}	nm*	As Cr^{6+}	Total chromium		
BS L16	3 minutes	440	150	29	190	43	16
BS L71		280	93	2.8	87	31	3
BS L16	9 minutes	570	190	46	250	43	18
BS L71		360	120	8.5	130	36	7
BS L16	27 minutes	960	320	62	360	37	17
BS L71		460	150	12	150	33	8

* Assuming a density of 3.0g cm^{-3}

Table 5

LABORATORY CORROSION TESTS ON BS L71 AND UNCLAD BS L88 TEST PIECES CHROMATE FILMED USING THE MARCHAND BATH

Material	Test	Coating and application parameters			Time to first corrosion (days)	Comments
		Type	Time (min)	Temperature (^{o}C)		
BS L71	Salt droplet	None			1	Badly corroded after 14 days.
		Anodized			25	Only one corrosion site.
		Chromate film	3	20	21	Only lightly corroded after 30 days.
			1.5	30	12	
			3	30	21	
	Salt fog	None			2h	Badly corroded after 1 day.
		Anodized			10	Only light to moderate corrosion after 30 days.
		Chromate film	3	20	5	Badly corroded after 7 days.
			1.5	30	5	
			3	30	7	Badly corroded after 10 days.
BS L88	Salt droplet	None			1	Badly corroded after 14 days.
		Anodized			None	
		Chromate film	3	20	30	A few small corrosion pits visible after washing test piece.
			1.5	30	20	Less than '0 small pits after 30 days.
			3	30	None	
	Salt fog	None			<1	Badly corroded after 5 days.
		Anodized			10	Only lightly corroded after 30 days.
		Chromate film	3	20	5-7	Badly corroded after 8 days.
			1.5	30	5-10	Badly corroded after 14 days.
			3	30	<14	

Table 6

NATURAL ENVIRONMENT CORROSION TESTS ON BS L71 AND UNCLAD BS L88 TEST PIECES CHROMATE FILMED USING THE MARCHAND BATH

Material	Test environment	Coating and application parameters			Time to first corrosion (weeks)	Comments
		Type	Time (min)	Temperature (^{o}C)		
BS L71	Rural	None			<1	Badly corroded after 4 weeks.
		Anodized			~26	Lightly corroded after 1 year.
		Chromate film	3	20	<1	Badly corroded after 4 weeks.
			1.5	30	<1	
			3	30	<1	
	Marine	None			<1	Badly corroded after 4 weeks.
		Anodized			1-2	Moderate corrosion after 1 year.
		Chromate film	3	20	<1	Badly corroded after 5 weeks.
			1.5	30	<1	
			3	30	<1	
BS L88	Rural	None			~18	Moderate to heavy corrosion after 1 year.
		Anodized			52	Corrosion on lower surfaces but only 10-20 sites.
		Chromate film	3	20	~26	Only lightly corroded on upper surfaces, but moderate to heavy corrosion on lower surfaces after 12 months.
			1.5	30	~26	
			3	30	~26	
	Marine	None			<1	Moderate corrosion after 8 weeks.
		Anodized			52	Corrosion on lower surfaces but only 10-20 sites.
		Chromate film	3	20	5-6	Only lightly corroded on upper surfaces after 8 weeks, but moderate corrosion on lower surfaces.
			1.5	30	2-3	
			3	30	4-5	

Table 7

THE EFFECT OF CONTINUOUS 5% NEUTRAL SALT FOG ON BS L71 TEST PIECES CHROMATE FILMED USING A DEPLETED MARCHAND BATH

Chromate coating conditions		Time to first corrosion (hours)	Comments (representative test pieces are shown in Fig.7)
Time (min)	Temperature (^{o}C)		
Uncoated		<2	Surface heavily corroded.
3	20	<69	About 10 corrosion sites if material within 4mm of edges is ignored.
3	25	78-93	>20 corrosion sites present, ignoring edges of test pieces.
3	30	93-96	>20 corrosion sites present, ignoring edges of test pieces.
9	30	96-99	Less than 10 corrosion sites.
27	30	102-117	Less than 10 corrosion sites.

Table 8

THE EFFECT OF CONTINUOUS 5% NEUTRAL SALT SPRAY ON TEST PIECES CHROMATE FILMED BY SPRAY AND SWAB APPLICATION OF MARCHAND SOLUTION

Material	Marchand bath concentration*	Surface orientation during application	Time of application (min)	Time to first corrosion (days)	
				Spray application	Swab application
BS L16	N	Horizontal	3	21	28
		Vertical	3	21	28
		Vertical	9	14	>30
BS L71	N	Horizontal	3	2	12
		Vertical	3	2	10
		Vertical	9	4	21
	C	Horizontal	3	3	10
		Vertical	3	3	13
		Vertical	9	3	13
BS L88**	N	Horizontal	3	10	21
		Vertical	3	4	21
		Vertical	9	4	10

* N = normal concentration of chromium trioxide (3.5g dm^{-3}), sodium dichromate (3.5g dm^{-3}), and sodium fluoride (0.8g dm^{-3})

C = concentration increased four-fold on all chemicals

** Cladding removed

Table 9

METAL LOSS DURING CHROMATE FILMING, AND THICKNESS AND CHROMIUM CONTENT OF CHROMATE FILMS OBTAINED BY IMMERSION IN PROPRIETARY PROCESS BATHS

Metal	Chromating process (temperature)	Average metal loss		Average chromate film thickness		Average chromium content of film $mg\ m^{-2}$	Weight % chromium in chromate film
		$mg\ m^{-2}$	nm	$mg\ m^{-2}$	nm*		
BS L16	X (20°C)	190	72	970	320	250	26
BS L71	X (20°C)	60	33	490	160	120	25
BS L16	Y (30°C)	530	170	1160	390	330	28
BS L71	Y (30°C)	410	150	620	210	180	29
BS L16	Marchand (30°C)	220	82	420 (440)**	140 (150)**	150 (190)**	36 (43)**
BS L71	Marchand (30°C)	320	120	340 (280)**	110 (93)**	55 (87)**	16 (31)**

* Assuming a density of $3.0g\ cm^{-3}$

** Values in brackets obtained without measuring metal loss (see Table 4)

Table 10

LABORATORY CORROSION TESTS OF BS L71 TEST PIECES CHROMATE FILMED BY THE MARCHAND AND BY TWO PROPRIETARY PROCESSES (X AND Y) USING EXPOSURE TO CONTINUOUS 5% NEUTRAL SALT FOG (SF) AND ALTERNATE IMMERSION (AI) IN 3.5% NEUTRAL SALT SOLUTION

Coating	Age of coating prior to test (days)	Test method	Time to first corrosion (days)	
			Plain side	Scratched side
Marchand	<1	SF	6-8	4
	12	SF	5	5
	<1	AI	4	4
	12	AI	5	5
X	<1	SF	6-8	6-8
	12	SF	5	5
	<1	AI	4	4
	12	AI	5	5
Y	<1	SF	6-8	4
	12	SF	5	5
	<1	AI	4	4
	12	AI	5	5

Table 11

ADHESION TESTS APPLIED TO PAINTED ALUMINIUM ALLOY TEST PIECES PREVIOUSLY CHROMATE FILMED USING THE MARCHAND PROCESS

Material	Marchand chromate filming conditions	Number of test pieces meeting classifications of cross-cut areas defined in BS 3900 part E6											
		Before exposure to salt fog						After exposure to salt fog for 30 days					
		Before tape test			After tape test			Before tape test			After tape test		
		0	1	2	0	1	2	0	1	2	0	1	2
BS L16	3 minutes at 30°C	3	-	-	3	-	-	2	1	-	1	2	-
	6 minutes at 30°C	3	-	-	3	-	-	3	-	-	1	2	-
	3 minutes at 40°C	3	-	-	3	-	-	3	-	-	1	2	-
BS L33	3 minutes at 30°C	3	-	-	3	-	-	2	1	-	2	1	-
	6 minutes at 30°C	3	-	-	3	-	-	2	1	-	2	1	-
	3 minutes at 40°C	3	-	-	3	-	-	3	-	-	2	1	-
BS L71	3 minutes at 30°C	3	-	-	3	-	-	2	1	-	-	3	-
	6 minutes at 30°C	3	-	-	3	-	-	2	1	-	-	3	-
	3 minutes at 40°C	3	-	-	3	-	-	3	-	-	2	-	1
BS L88*	3 minutes at 30°C	3	-	-	3	-	-	3	-	-	3	-	-
	6 minutes at 30°C	3	-	-	3	-	-	3	-	-	2	1	-
	3 minutes at 40°C	3	-	-	3	-	-	3	-	-	2	1	-

* Cladding removed.

Table 12

ADHESION TESTS APPLIED TO PAINTED BS L16 AND BS L71 TEST PIECES PREVIOUSLY CHROMATE FILMED USING TWO PROPRIETARY PROCESSES X AND Y

Material	Chromate filming process	Number of test pieces meeting classifications of cross-cut areas defined in BS 3900 part E6											
		Before exposure to salt fog						After exposure to salt fog for 30 days					
		Before tape test			After tape test			Before tape test			After tape test		
		0	1	2	0	1	2	0	1	2	0	1	2
BS L16	X	6	-	-	6	-	-	6	-	-	6	-	-
BS L16	Y	6	-	-	6	-	-	6	-	-	6	-	-
BS L71	X	6	-	-	6	-	-	1	5	-	-	5	1
BS L71	Y	6	-	-	6	-	-	2	4	-	1	5	-

REFERENCES

No.	Author	Title, etc.
1	W. Marchand	Chromate conversion coatings on aluminium. *Electroplg. Metal Finish,* 14, 439-447 (1961)
2	N.J. Newhard, Jr.	Conversion coatings for aluminium. *Metal Finish,* 70, (7), 49-53 (1972)
3	R.J. Sunderland	Analysis of chromate conversion coatings on aluminium. Proc. 6th Internl. Vacuum Congress (1974) *Japan J. Appl. Phys. Suppl.,* 2, (1), 347-350 (1974)
4	American Society for Testing and Materials	*Standard method of salt spray (fog) testing.* ASTM B117 (1975)
5	British Standards Institution	*Performance tests for protective schemes.* BS 1391 (1952)
6	Federal Supply Service	*Stress corrosion test for aluminium alloy plate, extrusions, and forgings by alternate immersion.* Federal Test Method Standard 151b, Method 823 (1967)
7	Ministry of Defence	*Cleaning and preparation of metal surfaces.* Defence Standard 03-2 (1972)
8	British Standards Institution	*Method of test for paints. Part E6. Cross-cut test.* BS 3900 (1974)
9	Ministry of Defence	*Chromate passivation of cadmium and zinc surfaces.* Defence Specification DEF 130 (1961)

Fig.1

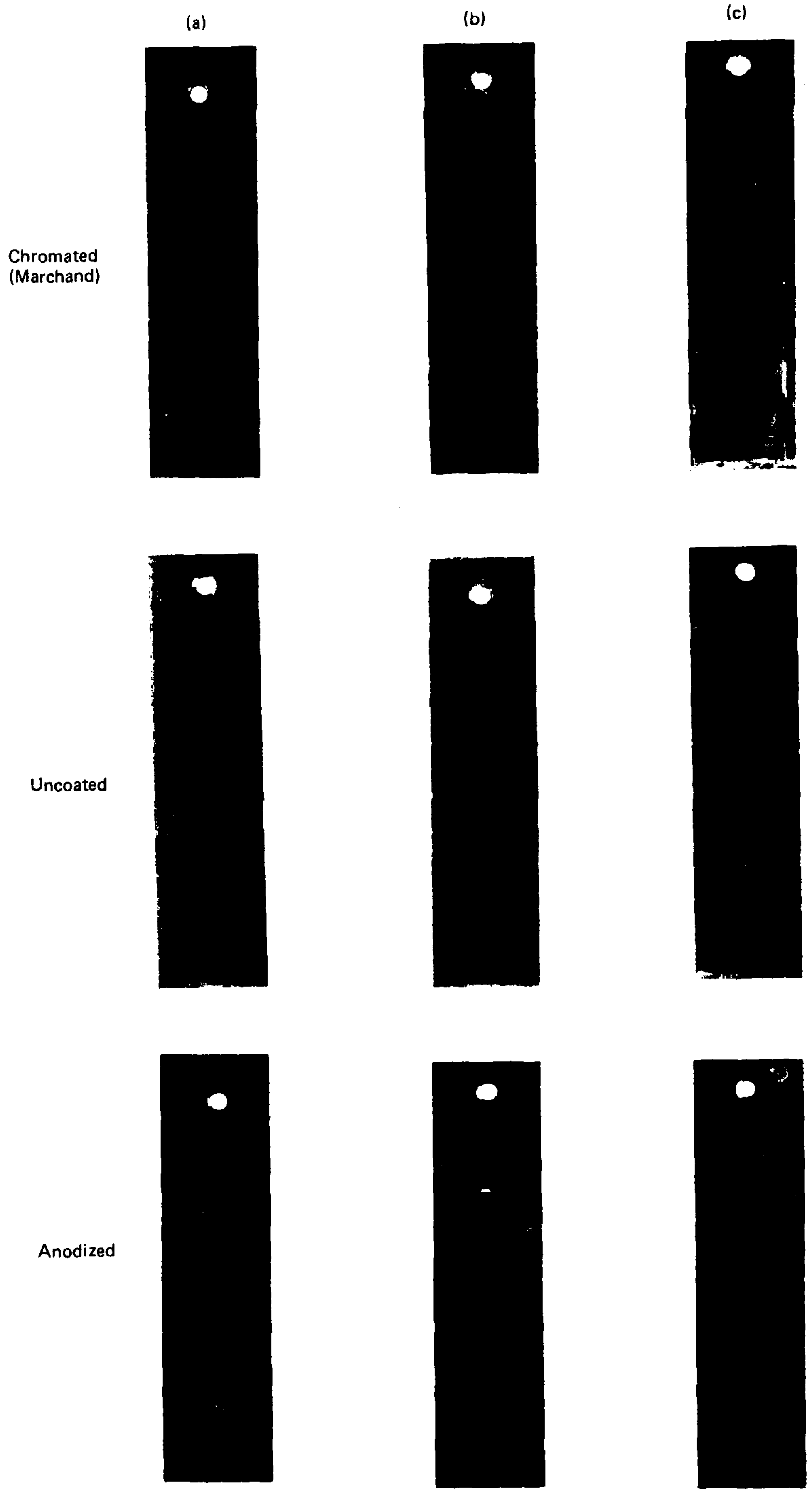


Fig.1 Protected and unprotected test pieces of BS L16 after exposure to (a) a rural environment for 1 year, (b) a marine environment for 1 year, and (c) a continuous 5% neutral salt fog for 30 days

TR 76063 C13416

Fig.2

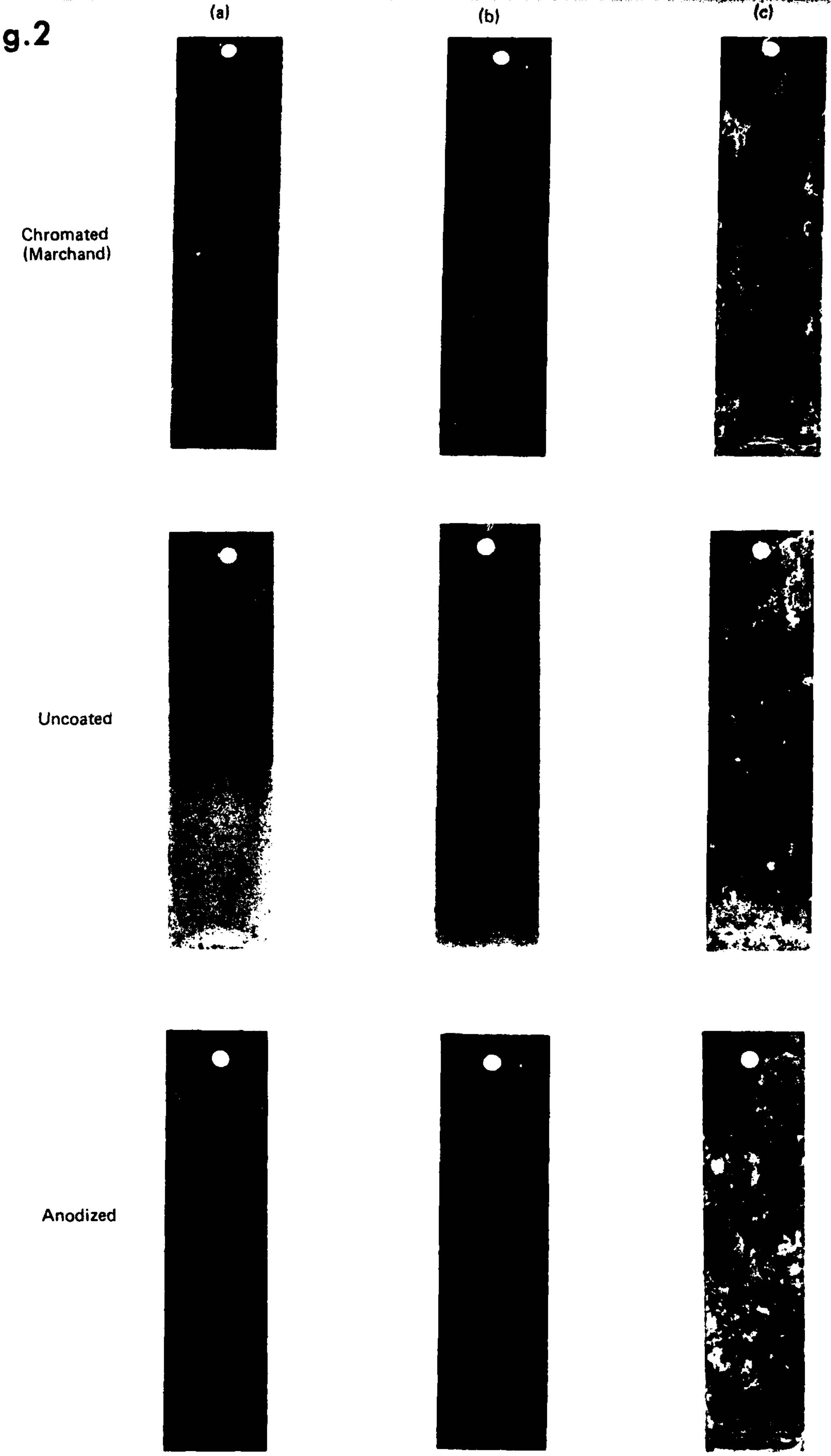


Fig.2 Protected and unprotected test pieces of BS L33 (machined faces) after exposure to (a) a rural environment, (b) a marine environment, and (c) neutral 5% salt fog

TR 76063 C13417

Fig.3

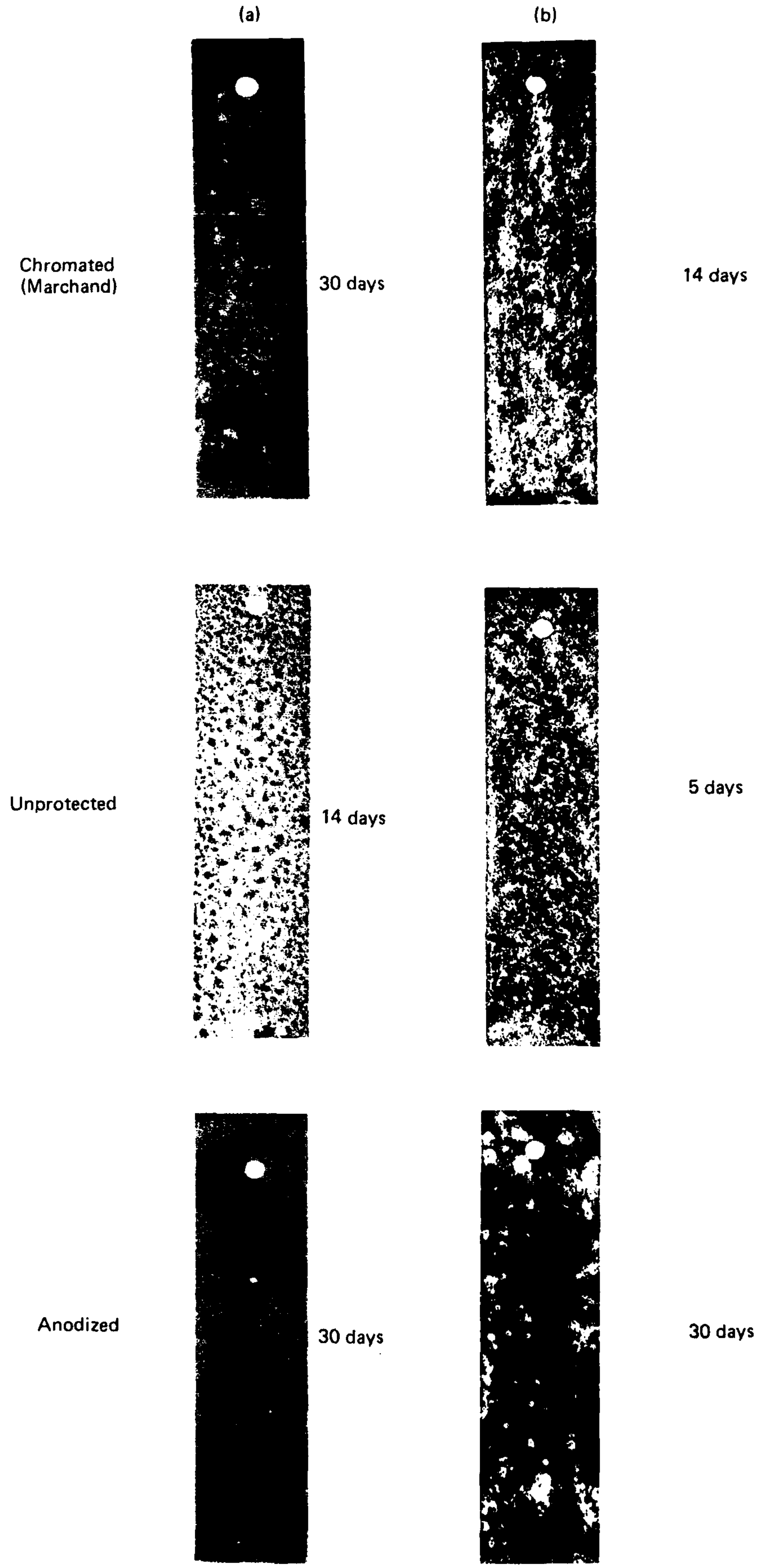


Fig.3 Protected and unprotected test pieces of BS L71 after exposure to (a) a salt droplet test, and (b) a continuous 5% neutral fog test

Fig.4

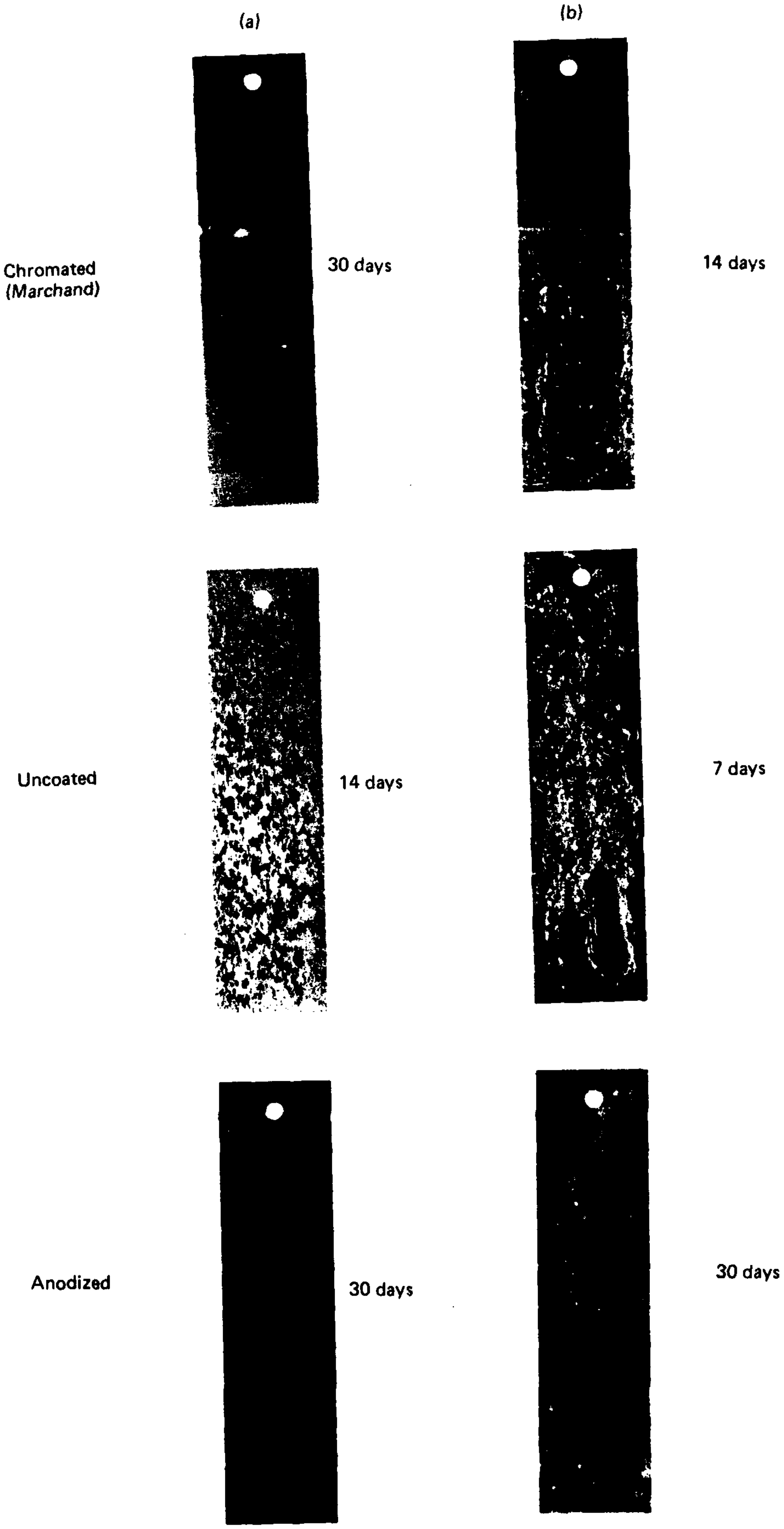


Fig.4 **Protected and unprotected test pieces of unclad BS L88 after exposure to (a) a salt droplet test, and (b) a continuous 5% salt fog**

TR 76063 C13419

Fig.5

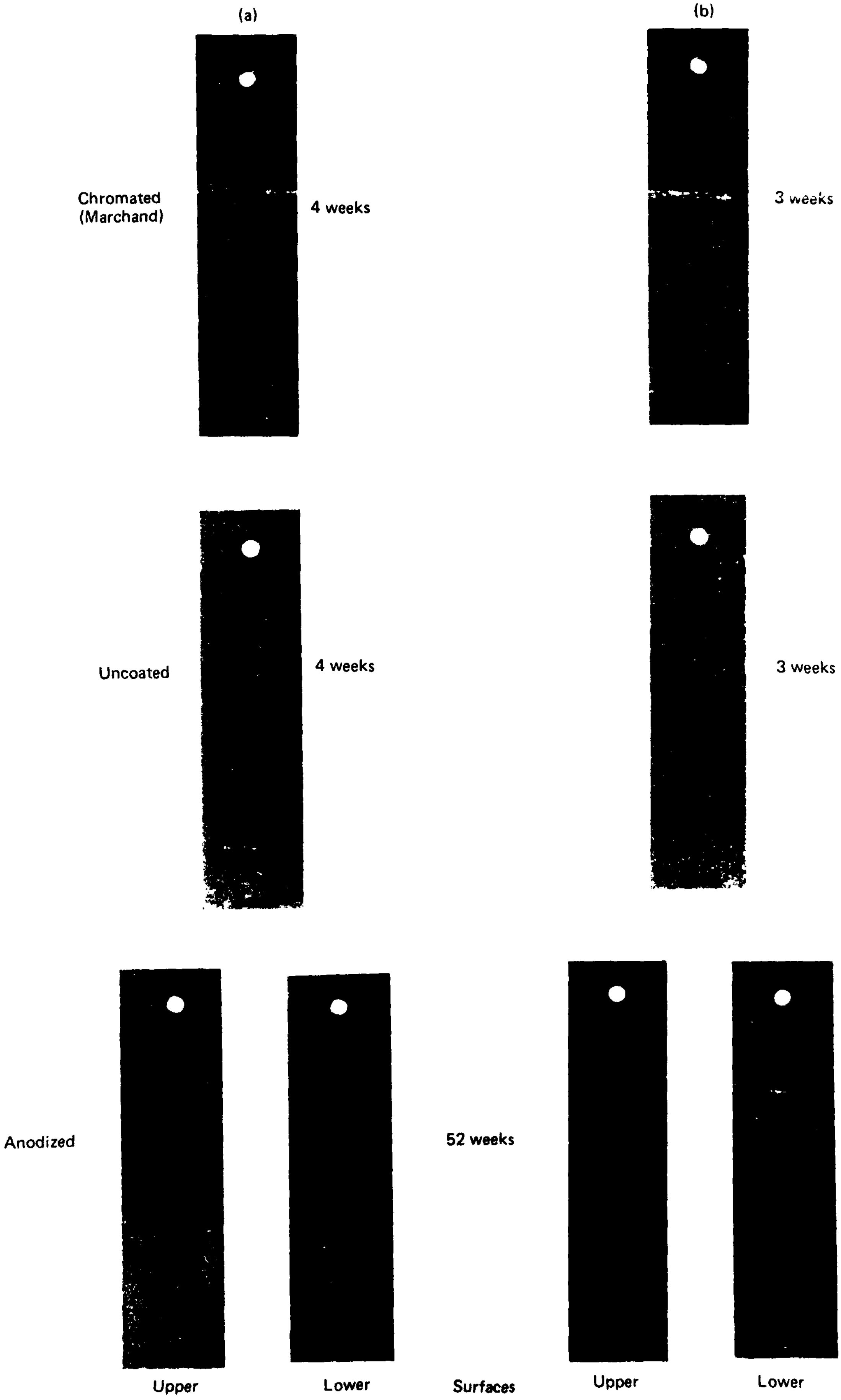


Fig.5 Protected and unprotected test pieces of BS L71 after exposure to (a) a rural environment, and (b) a marine environment

Fig.6

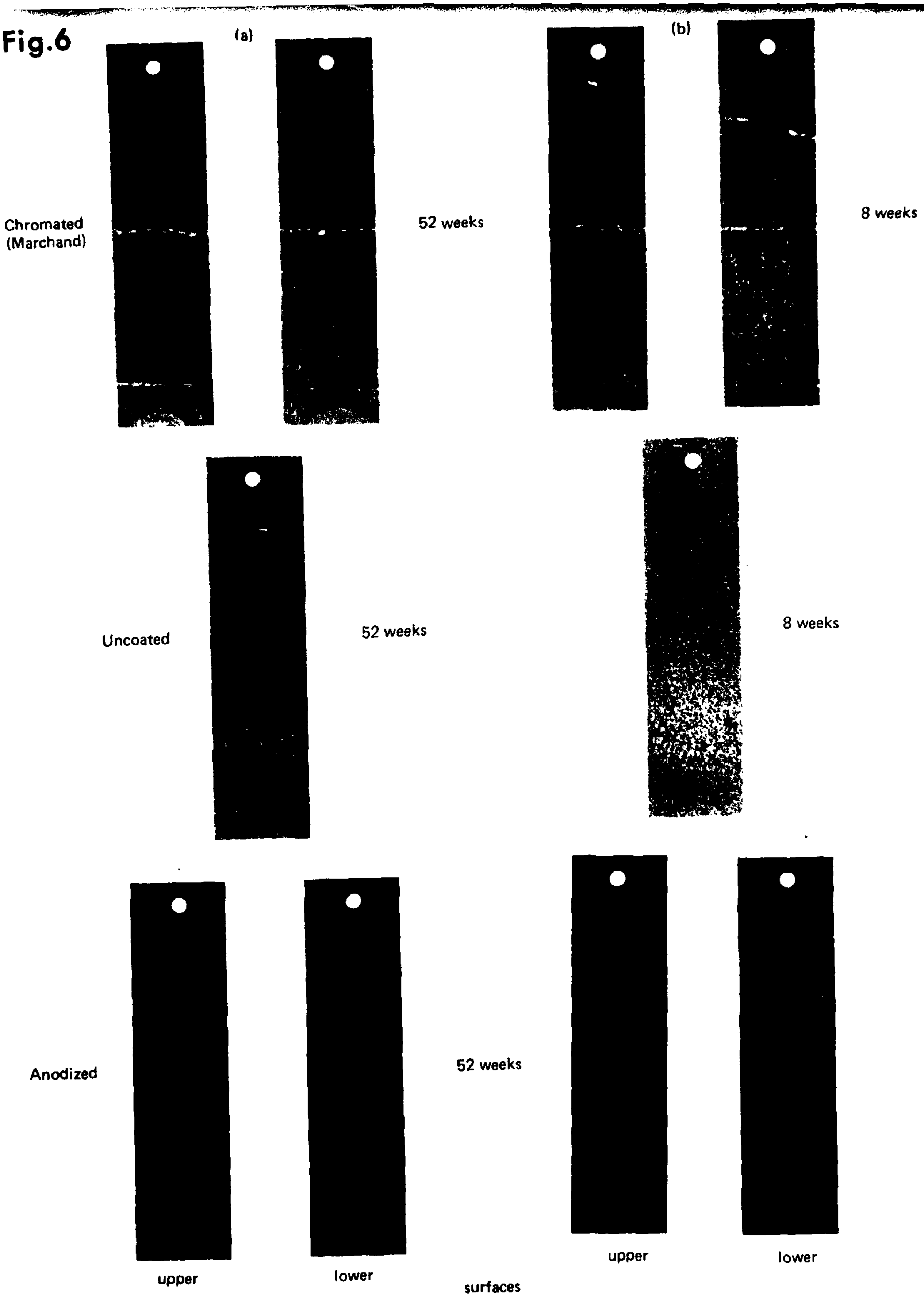
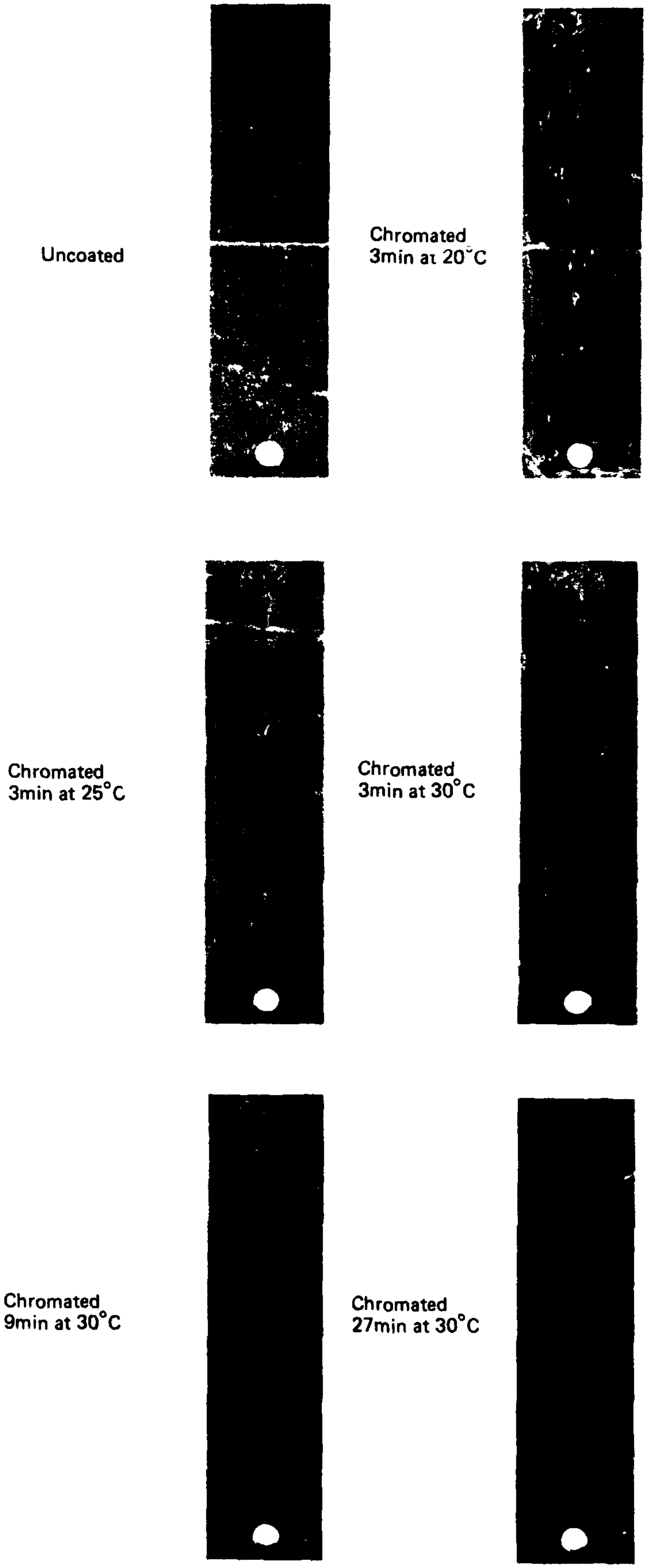


Fig.6 **Protected and unprotected test pieces of unclad BS L88 after exposure to (a) a rural environment, and (b) a marine environment**



Uncoated

Chromated
3min at 20°C

Chromated
3min at 25°C

Chromated
3min at 30°C

Chromated
9min at 30°C

Chromated
27min at 30°C

Fig.7 Test pieces of BS L71 chromate filmed with a depleted Marchand bath and exposed to continuous 5% neutral salt fog until first corrosion (see Table 7)

Fig.8

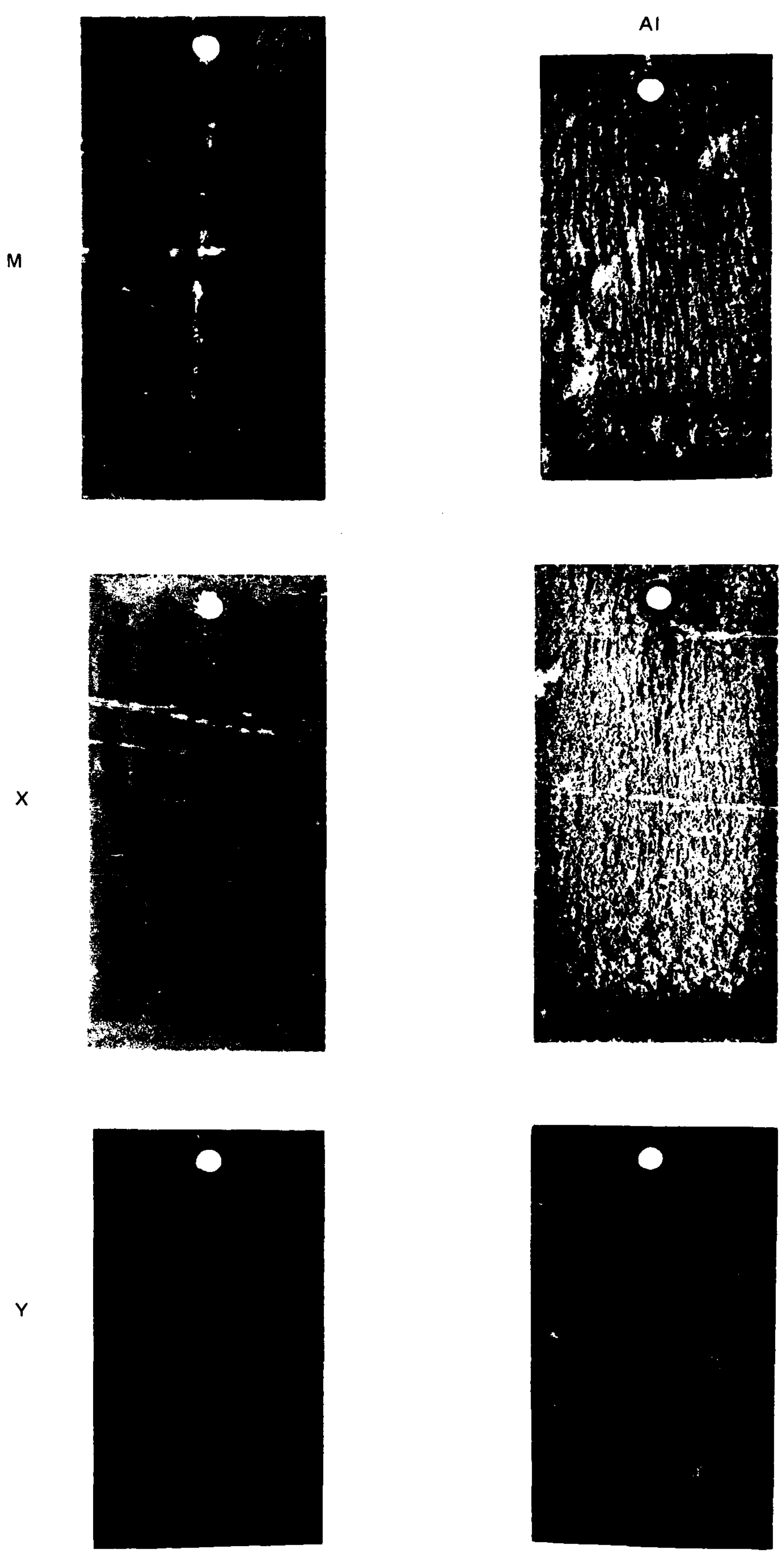


Fig.8 Test pieces of BS L71 chromate filmed by the Marchand process (M) and processes X and Y; exposed to continuous 5% neutral salt fog (SF) for 21 days and to alternate immersion in 3.5% neutral salt (AI) for 8 days

TR 76063 C13423

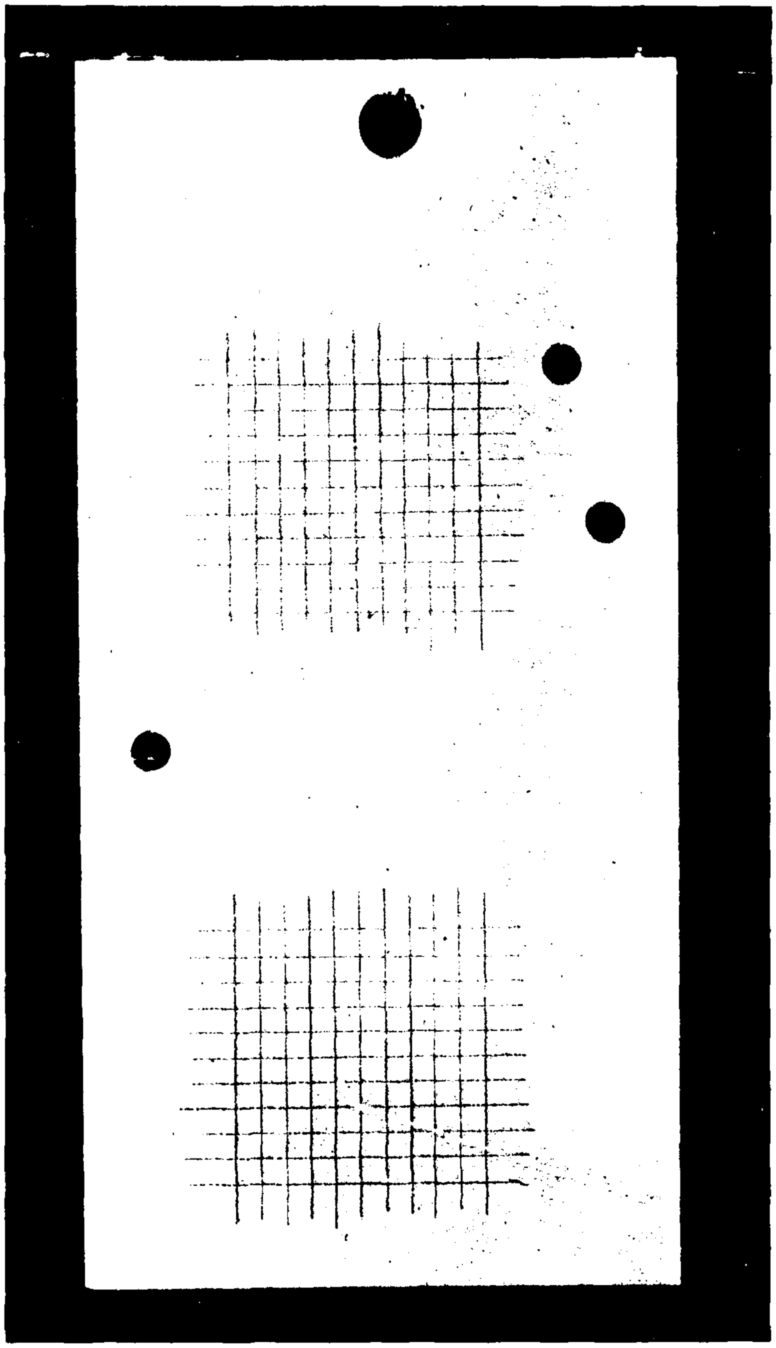


Fig.9 Cross-cut lattice patterns on a painted test piece

Fig.10

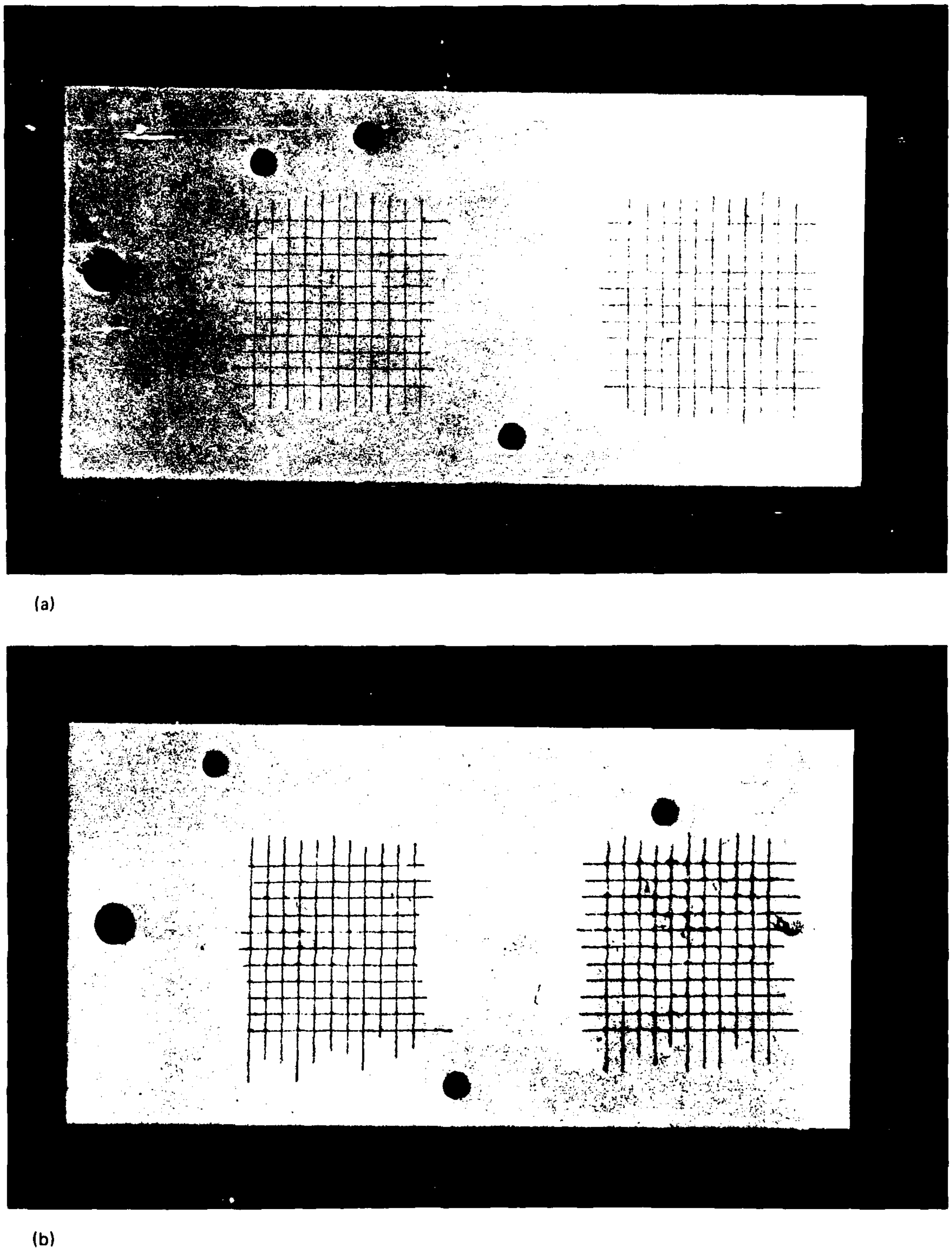
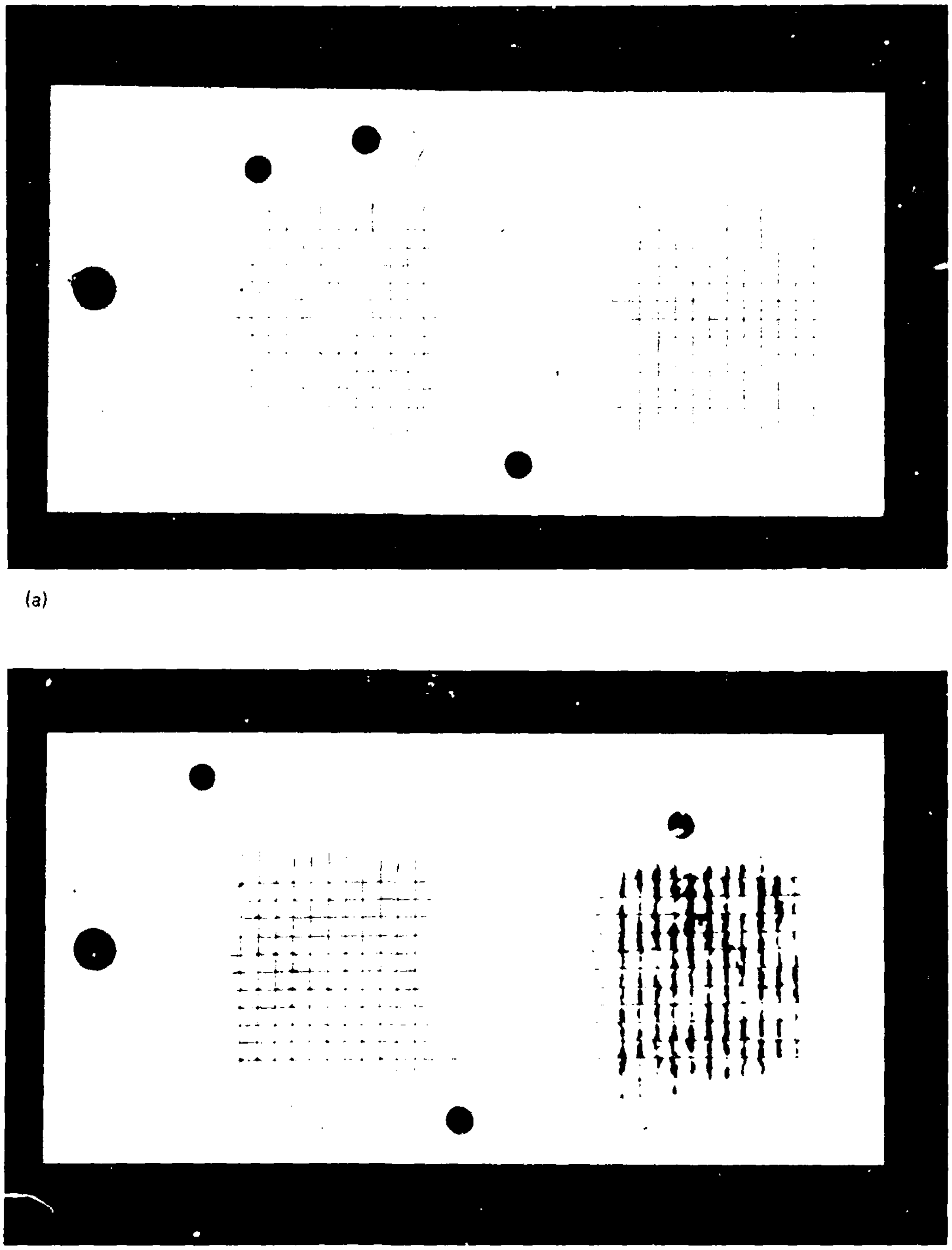


Fig.10 Cross-cut BS L71 test pieces after exposure to continuous 5% neutral salt fog for 30 days:
(a) a test piece showing no loss of paint, Classification 0
(b) a test piece showing loss of paint to Classification 1



(a)

(b)

Fig.11 Cross-cut BS L71 test pieces after exposure to continuous 5% neutral salt fog for 30 days and application of the cellulose adhesive tape test:
(a) a test piece showing no loss of paint, Classification 0
(b) a test piece showing loss of paint to Classification 2