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Failure mode and interface chemistry of localized coatings on brass

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The behaviour of partly coated aluminium brass has been examined under accelerated laboratory and under natural conditions. Acrylic (Incralac) coatings are found to have a good life and to provide a long-term protection of brass surfaces. Analysis of failed interfaces by photoelectron spectroscopy showed that acidic conditions developed beneath the coating and contributed to a partial weakening of the bond strength. Eventually the crevice conditions drift back towards neutral and there is little further loss of strength.

1. Introduction

The protection afforded by the mineral products on heat exchangers often breaks down at regions of high turbulence [1]. In the case of condenser tubes, these typically occur at a partial blockage of a tube by a piece of rock, shellfish or concrete from a culvert, as a result of air bubble entrainment; or indeed, as a result of poor hydrodynamic conditions at tube inlet or outlet. When this occurs, macroscopic pitting of the metal ensues so that even removal of the original blockage may not prevent ultimate failure of the tube at this point because of self-induced turbulence.

The case for some form of treatment of these sites is strong since the affected area may cover only 20 cm of a 20 m tube. We have thus investigated the use of organic polymer films for the treatment of such localized areas. In these circumstances the impact of the polymer film on heat transfer is unimportant. Vital requirements are excellent adherence and low permeability to water, together with resistance to undercutting, edge or crevice corrosion. The latter requirements are extra to those which are necessary for systems designed to coat the complete internal surface of the tube and the present paper reports an investigation into the failure mode of partly coated brass test pieces.

2. Experimental details

The work reported here was exclusively concerned with the behaviour of the acrylic lacquer, Incralac [2], supplied in clear, brushable form. Other polymer coatings were found inferior to Incralac under marine conditions [3]. The experimental programme was based on the measurement of adherence by a lap shear test, since this approximates to the type of loading applied to the films by the fast flowing water ($2\,\mathrm{m\,sec^{-1}}$). Samples measuring $100\,\mathrm{mm} \times 10\,\mathrm{mm} \times 1\,\mathrm{mm}$ were cut from slit and rolled tubes of aluminium brass (76% Cu, 22% Zn, 2% Al). The surface was prepared by abrasion to 240 grade silicon carbide paper, or by etching in 20% hydrochloric acid, rinsed and dried. Each test piece was prepared for exposure by coating a 20 mm length of one end of the strip with the test polymer using a bar coater to ensure uniform coating thickness of $33\,\mu\mathrm{m}$. The polymer was then allowed to set for the appropriate time. After setting, the edges of the test piece were ground to 240 grit giving a sharp demarcation between coating and metal, leaving every opportunity for lateral penetration of water. On the coated face the boundary between coating and metal was left in the original, feathered out state.

After exposure the adherence of the coating was measured by lap-bonding a dummy plate to the coated area of the specimen (Fig. 1). Cyanoacrylate adhesive was suitable for this purpose. The tensile strength of the couple was measured in a Houndsfield Tensometer using self-aligning, self-tightening grips. The surfaces, after failure, were examined for evidence of adhesive or cohesive failure and for evidence of corrosion

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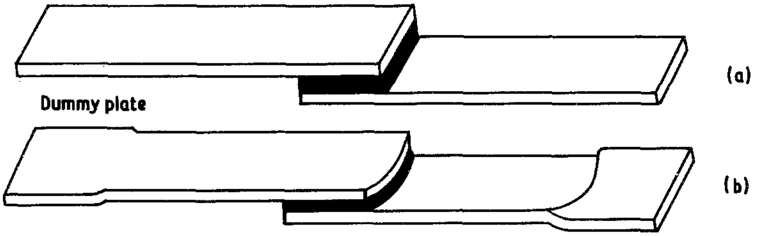

Figure 1 Lap-shear test assembly: (a) conventional; (b) corroded tube section.

undercutting the polymer film. The failed surfaces were examined by XPS (ESCA) in order to establish their chemical state and to determine the locus of coating failure after exposure to hot sodium chloride solution and natural seawater.

Both the metal surface and the equivalent surface of the detached lacquer were analysed. The spectra labelled "metal side" refer to the surface adhering to the metal after failure in a lap-shear test. Those labelled "lacquer side" are from the corresponding surface on the polymer film removed by the test.

A set of tests on the importance of cleaning was undertaken using test pieces cut directly from corroded tubes and tested without being rolled except for one end on which a flat was formed to permit mounting in the tensometer. The effect of poorly cleaned areas remaining to give crevices or faults to initiate failure was then investigated by cleaning limited areas, either transversely (Fig. 2a) or centrally (Fig. 2b). These were then coated over the entire 2 cm test length and bonded to a matching, curved, dummy plate when making the lap-shear test.

3. Exposure trials

Accelerated testing was undertaken by suspending the complete testpiece in 3% sodium chloride solution at 95° C. Samples were removed and tested to failure at suitable intervals of time. Short exposure to the hot sodium chloride solution had no noticeable impact on appearance or adherence of the coatings. Even after 10 days exposure to the accelerated test these coatings did not peel, nor was evidence of corrosion observed. The coated area steadily darkened during exposure and the abraded samples showed some evidence of dezincification of the outside edges of the coating.

4. Results

4.1. Adherence of lacquer

The load to failure, as measured by the lap shear test on duplicate specimens is given for the accelerated test in Table I. The figure for cyanoacrylate is included since it is important to note that the dry bond made to the dummy plate is stronger than the maximum bond strength exhibited by the test adhesive. The behaviour of the cyanoacrylate after exposure to test conditions is included for interest only and shows that this polymer has no value as a coating medium.

Duplicate samples were treated with two, four or six coats. Each coat was allowed to air dry for 1 h between successive applications. The results (Table I) show that a double coating confers a small advantage but further multiples of coats actually gave lower loads to failure at a given time. Examination of the latter test pieces suggested that interlaminar failure consistently occurred. Thus, although the test did not yield the true metal/lacquer adherence it was concluded that multiple coating would give no advantage to outweigh the practical difficulties of making several applications. The coatings on abraded surfaces did not develop the adhesive strength of the coatings on acid cleaned surfaces, as shown by one typical set of data in Table I.

4.2. Partly cleaned surfaces

The results are given in Fig. 3. On unexposed

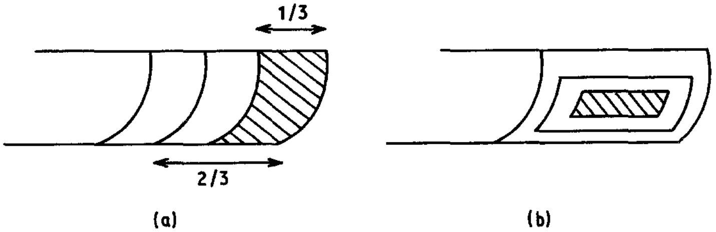

Figure 2 Transverse and central methods of surface cleaning: (a) transverse cleaning; (b) central cleaning.

TABLE I Failure load in lap-shear test

Coating type and number of applications	Load to failure (kgf)							
	Exposure to hot sodium chloride (days)							
	0	1	2	3	4	5	7	10
Cyanoacrylate (1)	245	20	–	–	13	10	–	–
Acrylic (1)	235	220	180	180	–	–	140	120
Acrylic (1)	235	–	–	–	180	–	–	–
Acrylic (2)	230	–	200	–	185	–	170	145
Acrylic (4)	180	–	150	–	130	–	120	110
Acrylic (6)	165	–	115	–	100	–	75	60
Acrylic + silane (1)	230	190	–	185	–	160	–	165
Acrylic, abraded surface (2)	100	95	100	–	70	80	97	97
	Exposure to seawater (months)							
	0	1	2	3	6	14		
Acrylic	235	230						
Acrylic + silane	230	–	210	200	196	170		

samples there was an increase in load to failure which was approximately proportional to the cleaned area. More important, however, was the finding that on a 3 day accelerated test any preformed crevice gave a greater than pro-rata reduction in load to failure. No visual affect could be attributed to the pre-existence of the undercut crevice and the uncleaned surface showed very little change on exposure.

4.3. Surface analysis

4.3.1. Surface before exposure

Spectra from the acid cleaned and the abraded surfaces of aluminium brass and from the lacquer itself are given in Fig. 4. Both brass surfaces show copper(I) and zinc ions at the concentrations given in Table II. The abraded surface is the cleaner from the evidence of the lower carbon concentration and the greater intensity of the metal ion peaks. The pick-up of organic contamination is a normal feature of immersion in aqueous solutions for cleaning or pickling and, as might be expected, chlorine is also present on the acid cleaned surface. Exposure to the atmosphere for several days caused carbon to increase relative to oxygen, and copper(II) compounds to overgrow both copper(I) and zinc oxides, and the abraded and acid cleaned surfaces become very similar (Table II). The carbon/oxygen ratio in the coating is similar to that on the uncoated metal substrates. Nitrogen in the lacquer is probably derived from the benzotriazol corrosion inhibitor.

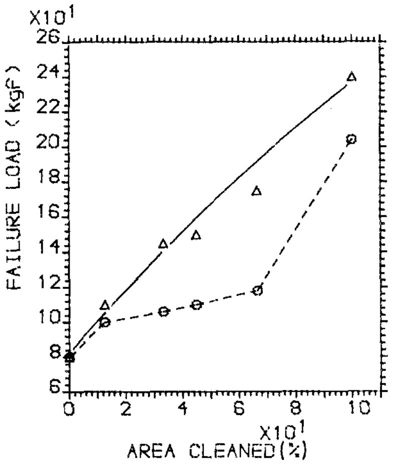

Figure 3 Influence of cleaning on failure load (——— unexposed, – – – – 3 days exposed, ▲ ● central cleaned).

In the present work the lacquer was applied to freshly prepared surfaces, i.e. they would be in the copper(I) state.

4.3.2. Interfaces exposed by lap-shear failure

The lacquer-side of interfaces exposed in the lap-shear test before the testpiece had been exposed to the sodium chloride solution were contaminated with a significant amount of copper oxide (Fig. 5a, Table III). This suggests cohesive failure within the oxide layer on the brass surface. After exposure both interfaces became contaminated with sodium and especially chlorine and the amount of copper oxide transfer diminished. Some zinc was usually found on the lacquer. The chloride concentrations (Fig. 5b) increased with exposure time up to a peak at about 4 days (Fig. 6). The value of this

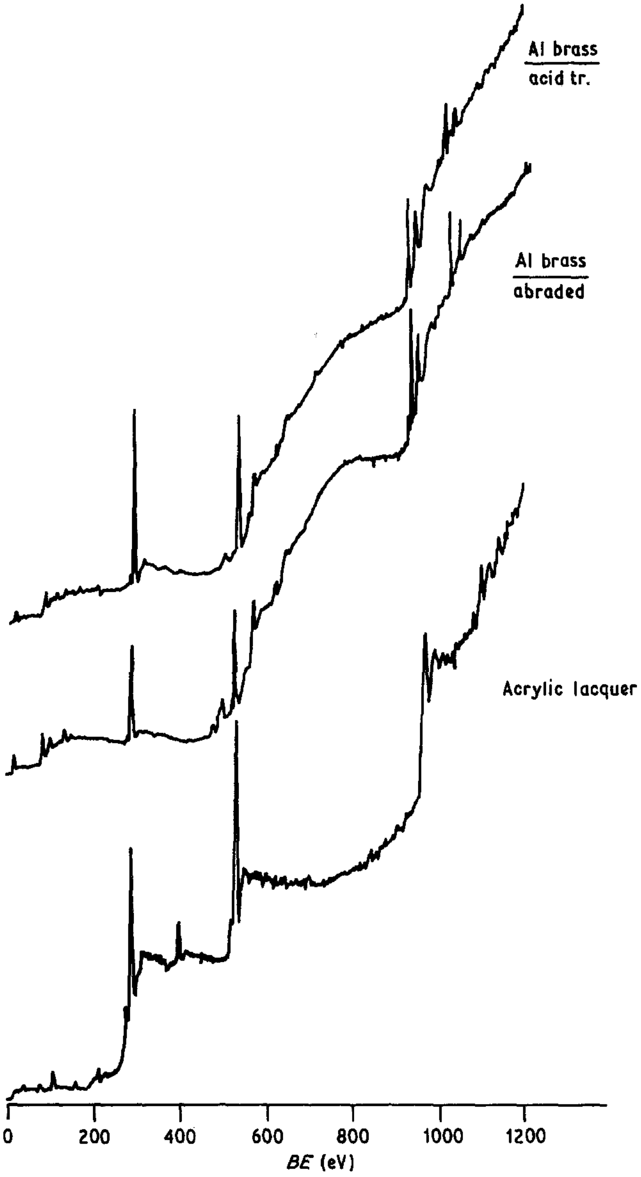

Figure 4 XPS (ESCA) spectra from the acid cleaned and the abraded surfaces of aluminium brass and from the acrylic lacquer.

TABLE II XPS (ESCA) results of acrylic lacquer and cleaned surfaces

at %	Acrylic lacquer	Abraded surface		Acid treated	
		Freshly prepared	Exposed to air	Freshly prepared	Exposed to air
C	63.2	60.4	68.6	67.9	70.1
O	25.7	27.8	25.2	25.9	20.8
Cu	–	7.5(I)	6.0(II)	3.0(I)	5.8(II)
Zn	–	4.3	0.2	1.4	0.2
N	6.9	–	–	0.8	1.6
Cl	2.3	–	–	1.0	1.4
Si	1.7	–	–	–	–

TABLE III XPS (ESCA) results (at %) of specimens exposed to hot sodium chloride solution

		C	O	N	Cu		Zn	Na	Cl	Si
Abraded surface: 1 coat										
M*	No exposure	74.1	20.4	3.1	0.4	(II)	0.6	0.7	0.6	–
	3 days	58.4	27.9	6.0	0.9		0.4	2.4	4.1	–
	8 days	66.6	22.9	3.0	1.5		0.8	2.2	2.9	–
L*	No exposure	65.3	25.5	6.6	1.5	(II)	0.2	0.1	0.8	–
	3 days	66.7	23.4	6.2	–		–	0.4	3.2	–
	8 days	66.6	22.6	7.0	–		0.6	0.6	2.5	–
Abraded surface: 3 coats										
M	1 day	67.1	16.8	1.2	0.3	(I)	0.5	–	11.6	2.4
	4 days	69.0	16.6	2.5	0.5		0.8	0.2	10.2	0.2
	10 days	67.0	17.4	4.1	0.3		0.3	–	10.7	0.1
L	1 day	69.5	19.0	5.7	0.2		0.3	–	4.9	0.4
	4 days	66.7	18.7	4.1	0.3		1.0	–	8.8	0.4
	10 days	66.6	17.7	2.1	0.1		0.5	0.2	12.6	0.2
Abraded and acid treated surface: 2 coats										
M	No exposure	71.1	19.0	8.6	0.3	(I)	0.1	–	0.3	0.7
	2 days	74.0	14.6	3.8	0.9		0.1	–	5.5	1.2
	4 days	67.1	17.5	4.8	0.3		0.1	–	9.6	0.6
	8 days	72.4	13.4	2.6	1.3	(II)	0.1	–	7.4	0.6
L	No exposure	76.6	10.9	10.3	1.0	(I)	0.2	–	–	1.0
	2 days	65.3	18.4	4.2	–		–	–	11.5	0.6
	4 days	65.2	15.1	1.8	0.2	(I)	–	–	16.1	1.7
	8 days	54.4	30.3	3.9	0.7	(II)	–	–	10.6	0.1
Acid treated surface: 2 coats										
M	No exposure	72.3	16.8	5.3	1.3	(I)	0.4	–	3.9	–
	2 days	68.4	17.8	4.2	1.1	(II)	–	–	8.0	–
	4 days	69.4	19.3	4.6	1.6		–	–	7.5	–
	8 days	68.6	16.4	2.8	5.2		–	–	6.9	–
L	No exposure	61.7	27.1	9.0	0.5	(I)	0.6	–	1.0	–
	2 days	61.7	24.3	5.4	0.9	(II)	0.1	0.2	7.2	–
	4 days	59.0	27.0	7.8	1.0		0.5	0.4	4.2	–
	8 days	52.0	36.0	6.6	0.8		0.3	0.7	3.5	–
1 thick coat (≃ 4 coats)										
M	No exposure	78.9	14.0	3.5	–		0.2	–	1.4	–
	2 days	69.0	18.7	3.5	–		0.02	–	8.1	–
	4 days	67.4	12.6	0.9	0.8	(II)	0.6	–	17.2	–
	8 days	65.0	21.0	4.0	–		0.1	–	9.9	–
L	No exposure	72.4	18.1	2.9	–		0.1	–	5.9	–
	2 days	69.2	18.7	4.1	–		0.2	–	7.7	–
	4 days	65.2	15.2	4.3	1.0		1.2	–	14.5	–
	8 days	66.1	21.1	5.2	–		0.1	–	7.3	–
1 thick coat; 6 months exposure to seawater at ambient temperature										
M		73.1	18.0	2.5	1.3	(II)	–	–	2.5	2.6
L		65.5	27.1	1.9	0.9		0.3	0.4	2.3	1.6

*M = metal side; L = lacquer side.

peak concentration increased with coating thickness (Fig. 7), and appeared to be independent of surface preparation. Both the lacquer-side and the metal-side of the failed interface had similar concentrations. By contrast the sodium concentration decreased with coating thickness (Fig. 7), and increased with time of exposure instead of peaking at 4 days. No difference in surface analysis was found that could explain the difference in adhesion to the acid etched and the abraded surfaces.

5. Discussion

The Incralac formulation is not intended, nor recommended by INCRA for use under immersed conditions. For the application considered here, however, it appears to have a good deal to recommend it. In particular, it did not peel, nor allow undercutting corrosion; was satisfactory with a single application, retained good adhesive and cohesive strength after a very rigorous test and was tolerant of variations in initial cleaning

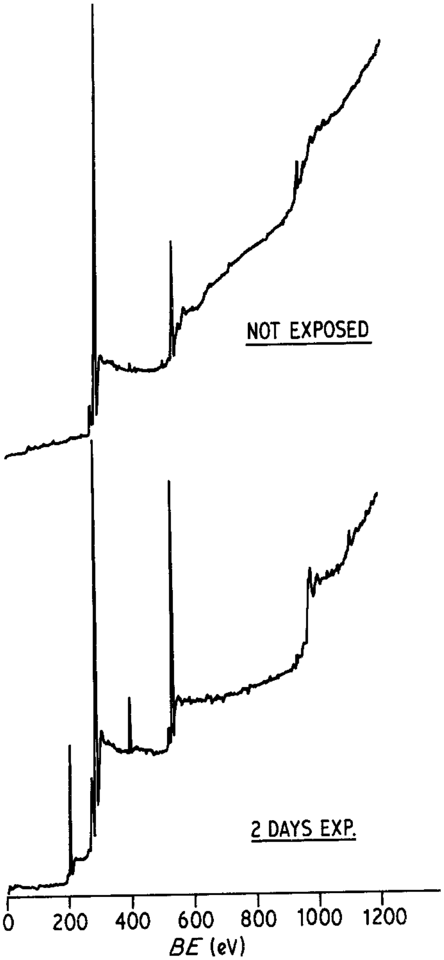

Figure 5 The lacquer side of interfaces exposed in the lap-shear test (a) before exposure, (b) after exposure to hot sodium chloride solution.

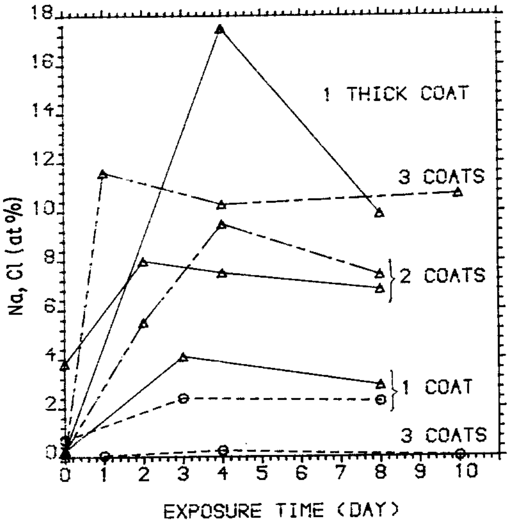

Figure 6 Chloride and sodium concentration on metal side of interfaces exposed in the lap-shear test (○ sodium, △ chloride, ct = coating, abr. tr. = surface abraded, ac. tr. = acid treated).

procedure, including the presence of uncleaned areas. The test used was designed to simulate and if possible accelerate several actions of natural seawater. These are (a) lateral penetration of water from the exposed edge of the coating with consequent debonding, (b) crevice corrosion at the periphery or within the coated area, and (c) cathodic disbonding resulting from anodic activity in the adjacent uncoated regions. In considering the results it is necessary to identify which of the above actions was responsible for the weakening of the adhesive bond and to establish that this is a realistic acceleration of the natural process.

None of the samples showed evidence of a progressive disbonding from the edges of the coated area as would be expected from water alone. Also the very significant concentrations of sodium and chloride ions implies that the solution had access to the interface in all cases. Thus the action of water itself can be dismissed. Of the other

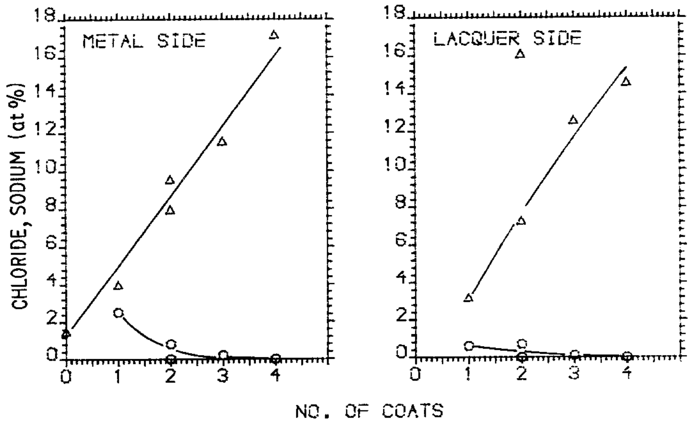

Figure 7 Peak concentration of chloride and sodium relative to coating thickness (▲ chloride, ○ sodium).

two possibilities crevice corrosion is an anodic activity and leads to the accumulation of chloride ions within the crevice [4] whilst cathodic disbonding is recognizable by the accumulation of sodium ions [5]. From the results presented in Figs. 6 and 7 it is clear that the system is behaving as an anodic crevice. The localization of anodic activity within the crevice was enhanced by increasing the thickness of the lacquer exactly as would be predicted. After some 4 days the chloride concentration tended to diminish and sodium concentration began to rise. This was most marked on the thin coat and less so on the thick coats. The clear implication is that after this time the intensity of electrochemical segregation within the crevice is fading, either because of an opening of channels within the interface or because of developing porosity across the polymer. The influence of coating thickness supports the latter conjecture. The load to failure declined much less rapidly once the sodium concentration began to increase.

The potential beneath a coated region of metal depends on its relationship to the adjacent uncoated area. The usual situation is for the sub-coating interface to be cathodic and hence alkaline. On a steel, for example, exposed metal corrodes readily whilst many of the polymers used in paints transmit oxygen sufficiently well for the coated area to act as a cathode. The reversal in the present case probably stems from the inhibition of the exposed, uncoated, brass by the pre-existing corrosion product. The good performance of lacquers on acid-cleaned surfaces may arise because the bonds formed are with acidic groups on the surface and hence resistant to acid hydrolysis.

Because acid disbonding is rather unusual it is especially important to compare the accelerated test with the natural process. Samples were exposed to natural seawater in a laboratory container but the load to failure at ambient temperature was unchanged after 30 days. Subsequently, therefore, samples coated with Incralac (slightly modified by addition of 3% of an ethoxysilane) were exposed for up to 14 months (Table I). A slow deterioration in bond strength could then be seen and analysis of the failed interfaces showed precisely the same pattern as emerged from the accelerated test (Table III), i.e. divalent copper, zinc transfer to lacquer side, high chlorine and trace of sodium. Thus we conclude that crevice corrosion also ensues in natural conditions and that the test used was a valid means of accelerating attack. Comparison of the deterioration rates of the coating suggests an acceleration by about one hundredfold. Thus lifetimes of several years are predicted. This is now supported by trials in power station service.

6. Conclusions

When aluminium brass is partly coated and exposed to seawater the interface becomes an anodically active crevice. The build-up of a corrosive environment is self limiting, possibly because transport across the polmer film makes the crevice imperfect. The adherence of the coating remains good and the load to failure reaches a plateau after the initial drop associated with the most intense electrochemical activity.

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