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Preliminary investigation into the application of scratch testing to marine coatings

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Controlled scratch testing has been applied to experimental coatings of the kind used on marine structures, based on epoxy-amine resins. Measurements of the scratch hardness and the critical load to failure have been made. Inspection of the scratch tracks by reflected light microscopy and scanning electron microscopy enabled identification of the failure mechanism. Failure could be by though-thickness cracking or adhesion failure. The failure mechanism is sensitive to the coating thickness and detachment from the substrate was obtained only from coatings less than 300 μm thick in the as-prepared state for tests conducted with a limiting load of 80 N. The deterioration of properties of samples immersed in hot seawater was very sensitive to composition.

1. Introduction

Marine coatings are applied to provide corrosion protection for the substrate. They are subjected to quite exacting, yet predictable, conditions in service and are required to have lifetimes measured in years rather than weeks. It is therefore important to have accelerated test methods to characterize new coating compositions. Marine coatings have quite complex formulations to meet the rather wide range of property requirements, which include particular mechanical properties; barrier properties; adhesion to the substrate; anti-fouling; resistance to collision damage; and a fairly wide temperature range. It should be noted that tanks may require linings that are resistant to hot oil (with temperatures up to 80°C) and cold sea water (used as ballast) as well as being capable of surviving collisions with solid cargo.

One problem that has been identified with marine coatings (and shared by many other coating systems) is the development of internal stresses. These can occur when a coated steel plate suffers a drop in temperature (for example, when a ship moves from an equatorial region to a polar region, or at the end of a period in dry dock in a hot climate) causing the coating to attempt to contract much more than the steel, which has a much smaller coefficient of thermal expansion. The steel has a much higher elastic modulus than the coating and is usually much thicker, and as a consequence, the coating is put into tension. This may lead to cracking or detachment, the principal mechanisms of coating failure. The internal stresses are also affected by swelling if water is absorbed by the coating or by volumetric changes if a component (such as an antifouling agent) is leached out. Adhesion to the substrate may be reduced if water penetrates to the coating-substrate interface.

In a scratch test, a stylus of well-defined dimensions is pressed against the sample that is then drawn past it, usually at a constant speed. To maximise the information obtained, the normal force pressing the stylus against the sample is increased in a controlled manner. This type of test is fairly well established in the characterization of hard coatings (such as titanium nitride coatings on stainless steel) but a full quantitative analysis is not currently available [1]. It has not found the same level of acceptance in the characterization of soft (polymeric) coatings [1, 2]. The test is likely to cause detachment of the coating from the substrate and the normal force at which this happens for a particular combination of stylus shape and dragging speed may be used to characterize the coating-substrate adhesion. The nature of the deformation around the scratch may provide information about the condition of the coating and will be influenced by its Young's modulus and ductility. Discussion of the mechanics and the failure modes that are observed in scratch testing relates mainly to hard coatings [1–14].

In the work described here, examples of experimental marine coatings have been conditioned in water in the laboratory and then subjected to a scratch test after varying periods of drying out. It should be noted that, in addition to the change in Young's modulus and ductility that occurs on drying out, loss of water will cause shrinkage and, therefore, the formation of tensile internal stress, and that this happens when a ship is in dry dock.

2. Experimental

2.1. Materials

The materials used were experimental compositions of the kind used for marine coatings and were provided

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TABLE I Coating preparations

Coating	Composition	Thickness (μm)
A	Hydrocarbon-modified epoxy-polyamide with extender pigmentation	200 ± 20
B	Epoxy-amine adduct with aluminium pigmentation	500 ± 32
C	Liquid epoxy-amine with extender pigmentation	900 ± 100
D	As C but unpigmented and almost solvent free	1200 ± 100
E	As C but unpigmented and solvent thinned with 20 wt% xylene/butanol (3 : 1)	200 ± 10

by Akzo-Nobel (International Paint), Felling, Tyne and Wear, UK. They were all two-component epoxy-amine systems designed to cure under ambient conditions. The compositions are summarised in Table I. A quite wide range of solids : solvent ratios was represented. Coating A had 75% solids by volume and contained an unreactive, medium molecular mass hydrocarbon diluent, to reduce viscosity, and extender pigmentation (mica or talc) to improve barrier protection. Coating B had 55% solids by volume, including aluminium flake as part of the pigment package. The low molecular weight, multifunctional amine adduct was chosen to react effectively with the epoxy resin to minimise volatilisation and corrosive reactions associated with low molecular mass amines. Coating C contained 85% by weight solids. Coatings D and E used the same resin system as C: Coating D was almost solvent-free (5% solid by weight) whereas Coating E was thinned by the addition of 20% by weight of a mixture of xylene and butanol (3 : 1).

2.2. Preparation of the coatings

The components were mixed using a simple paddle mixer then allowed to stand for periods between 7 minutes and 82 minutes before application. The shim steel substrates (150 microns thick) were cleaned using solvent prior to the application of the coating. The coatings were deposited using a doctor blade technique that produced uniform thickness coatings between 0.2 mm and 1.2 mm thick. The coatings were allowed to cure for at least three months prior to scratch testing or immersion in water for the study of the effect of conditioning. This period of time is sufficient to stabilize residual stresses that occur as the result of solvent removal [15].

2.3. Conditioning procedures

Coated shims were placed in a beaker of unstirred seawater held at 60°C for 24 hours. Some corrosion of the uncoated surface of the steel occurred and attack at the coating-substrate interface was evident but the centre of the sample was visually unchanged after exposure. The visually unchanged area was large enough to perform scratch tests and was used for the experiments that are reported below.

Immersion in (sea) water and drying out causes changes in the internal stresses in coatings [16, 17]. Rapid changes in stress occur immediately after removing the coating from the water bath and the execution of the scratch test was delayed until the coatings stabilised somewhat. To minimise any effect related to internal stresses, a delay of one hour before conducting the scratch test was adopted as standard. The samples were held vertically during this period to assist water run off and drying.

2.4. Scratch testing

The scratch tests were made using a Rockwell "C" diamond stylus (120° cone with a 200 μm diameter tip) under continuously increasing load using a spring-loaded automatic scratch tester. The loading rate was set at 100 N/min and the specimen table speed was 10 mm/min, giving a loading ramp of 10 N/mm along the scratch track. The load ramp was continuously monitored and recorded to check that the control settings were faithfully followed. The tests were terminated at one of three maximum loads: 40 N, 60 N or 80 N. The terminal point gives a clear impression from which measurements can be made along the scratch track, so calibrating the normal load at each location. This calibration can then be used to determine the load at which any visibly identifiable critical event occurs.

The test rig used for scratch testing allows measurement of the drag force as well as the normal force, so that the coefficient of friction, μ, can be monitored continuously and obtained as a function of load.

2.5. Analysis of scratch tracks

The scratch tracks were inspected by reflected light microscopy and scanning electron microscopy (SEM). SEM samples were sputter-coated with gold to minimise radiation damage and charging. The general appearance of the scratch tracks is illustrated by Fig. 1. This shows a scratch track on a sample of Coating A. The stylus was lowered onto the surface at the right hand end of Fig. 1, then the sample was dragged from left to right under the stylus. The test ended when the load reached 80 N; at this time the stylus was at the left hand end of the track, at the left hand side of the field of view in Fig. 1. The semi-circular front is clearly defined at the terminal end of the track and the axis through the centre of the stylus is easily located, so enabling the calibration of the load-position relationship referred to in Section 2.4.

The track images were used to determine the track width, d, at various selected loads. These data were used to calculate the scratch hardness, H_{scr}, given by [18]:

$$H_{\mathrm{scr}} = \frac{4kL}{\pi d^2} \tag{1}$$

where L is the normal load and k is a constant determined by the (inverse of the) fraction of the projected semi-circular contact area that is actually in contact with the stylus. There is no convenient method to obtain k and it has been assumed in this work that $k = 1$, i.e., that there is contact around the whole of the area of the stylus that penetrates the surface. This requires that, at the dragging speed used, viscoelastic recovery behind the stylus is rapid enough to maintain contact with its trailing surface. It is unlikely that this will happen

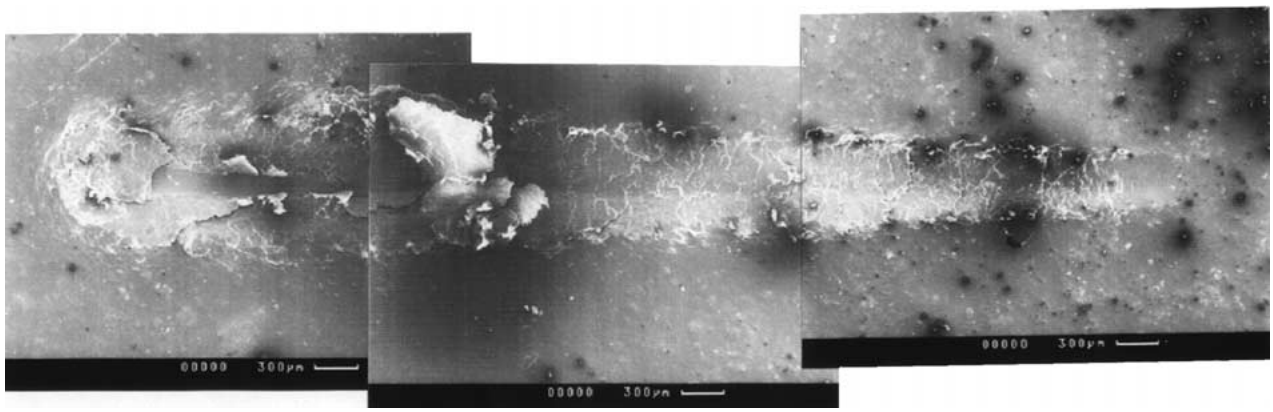

Figure 1 Scratch track on a sample of coating A showing the terminal point (at load 80 N) at the left hand side.

completely and the contact area will be rather less than complete and, correspondingly, the true scratch hardness of the sample will be underestimated, but is unlikely to introduce serious error in coatings with low elastic modulus as examined here. In tests on metals and ceramics the load is supported on the front half of the stylus only because plastic deformation prevents recovery, and contact is lost behind the stylus giving values for k closer to 2.

3. Results

3.1. General scratch test characteristics

The coefficient of friction did not vary much with load once the scratch was established, and for the series of coatings examined here μ fell between 0.2 and 0.25 in most of the tests performed. A simple estimate of the tensile stress generated in the coating behind the moving stylus can be calculated by dividing the frictional force by the cross-sectional area of the scratch track (which is obtained from the track width and the stylus geometry). The maximum tensile stresses measured in this way are of the order of 100 MPa for all samples. This is much larger than the residual stresses in the coatings (generally of the order of 1 MPa and rarely greater than 10 MPa, e.g., see Gu Yan and White [15, 16]). Therefore it is not surprising that cracking occurred during scratch testing in coatings that showed no sign of cracking in response to curing stresses or internal stresses produced by the conditioning procedure. The tensile stress values in the film behind the stylus calculated by this method must be regarded as approximate because there is, as yet, no good model for scratch testing of a bulk solid that plastically deforms, and a coating-substrate combination is even more difficult to analyse.

The scratch hardness was evaluated at 40 N normal load for all samples. At this load the stylus did not penetrate through even the thinnest coatings in this study, and any influence of the substrate can be neglected. Evaluations were also made for other normal loads for selected tracks. The data obtained at 20 N were in good agreement with those obtained at 40 N except when early onset of detachment was present at the higher load. Widely different values for hardness were obtained when evaluated for higher normal loads for which detachment was well advanced.

3.2. Failure modes in coatings aged in laboratory air

Two major modes of coating failure are produced by scratch testing: cracking in the through-thickness direction; and adhesion failures. For convenience, the cracks in the through thickness direction are called "through thickness cracks" from now on, though with the thicker coatings it is not usually possible to say whether they actually penetrate to the interface with the substrate. Observations on the 200 μm thick coatings indicate that the through thickness cracks do penetrate through to the interface.

The mode of failure observed depends on the properties of the coating, the coating-substrate adhesion, the geometry of the stylus, and the mechanical and kinematical conditions applied in the test. The results reported here were obtained on regions of coatings that were free from visual defects: because of the opaque nature of the filled coatings it was impossible to be sure that no defects were present in the interior of the coating or at the coating-substrate interface. In a few cases in which coating detachment occurred during scratch testing, it was found that defects such as voids were revealed to be present at the interface between coating and substrate when failure occurred. Information and data from these tests are not included below. In addition to through-thickness cracking or adhesion failure, there are secondary effects that can sometimes lead to a more comprehensive characterization of the scratch test.

Scratch tests on unfilled resin samples gave examples of both modes of failure with thin coatings. With the introduction of pigment or filler, through-thickness cracking became more probable. It was deduced that the cracking was caused by the tensile stresses behind the moving stylus. They tended to form at quite low loads. When the load was sufficient for the stylus to penetrate to depths close to the full coating thickness, coating detachment could occur. For the experiments reported here, with a maximum load of 80 N, this means that detachment was observed only for those coatings less than $\sim$300 μm thick. The mechanism for detachment is illustrated schematically in Fig. 2. A through-thickness crack behind the stylus penetrates to the coating substrate boundary (Fig. 2a). Further motion of the stylus causes the coating ahead of it to slide across the substrate; the pile-up of material ahead of the

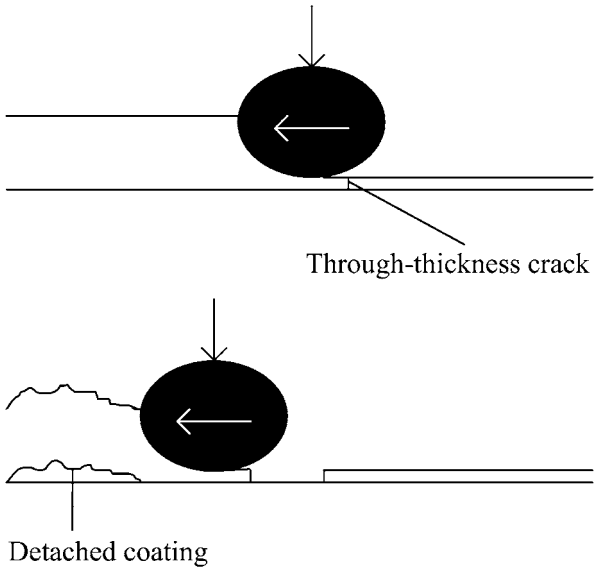

Figure 2 Schematic of the mechanism of detachment.

stylus is partly relieved by detachment of the coating (Fig. 2b).

Another type of through-thickness crack, observed with thicker coatings, was the so-called "conformal crack" which formed as the coating bent to follow the shape of the stylus. These cracks are related to those that are promoted by an indentation made with an indenter moving only in the normal direction and with no sliding. They started near the centre of the track and followed the curvature of the stylus. The sliding motion caused a secondary effect and the cracks became distorted into both forward and backward directions (Fig. 1). When forward- and backward-cracks intersected, small regions of the coating could become detached in a spallation-like event, as in Fig. 3, in which the detached zone clearly does not reach down to the interface with the substrate. This type of detachment is quite different in appearance from that caused by the mechanism described earlier (as illustrated in Fig. 2). No gross spallation occurred.

In some coatings, neither cracking nor detachment was observed. In this case the scratch track was characterized by piled-up material on either side. This contained markings that could be mistaken for cracks but which, on careful inspection, were seen to consist of folded material, evidence for significant plasticity. Fig. 4 shows an example of this on a sample of coating E.

Another simple, yet potentially informative, observation was recorded at the end of each scratch test and that was the appearance of the stylus diamond. In some cases part of the coating was removed when the stylus was lifted from the sample surface, remaining attached to the diamond. When this happened, the impression at the terminal end of the track showed characteristic markings where small fragments had torn away without involving deep cracking within the coating (Fig. 5). This indicates that the cohesive strength of the coating is less than the adhesion strength of the coating-diamond interface.

The results of the scratch hardness measurements are given in Table II. Through thickness cracks appeared at relatively low loads. The critical loads recorded in Table II are those at which the first recognisable failure other than through thickness cracking occurred.

3.3. Effect of coating thickness

As noted in Section 2.2, Coatings D and E differed only in the solvent content in the mixtures prior to curing

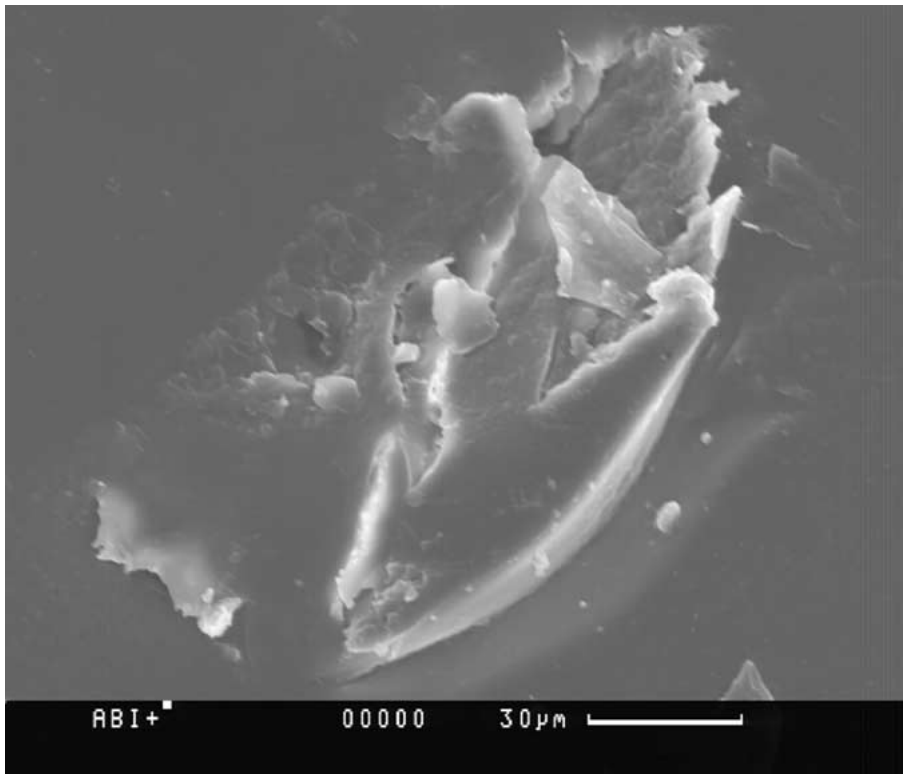

Figure 3 Spallation on a sample of coating E.

TABLE II Test measurements on as-prepared coatings and seawater-conditioned coatings

	As-prepared			Seawater-conditioned	
Coating	Scratch hardness (MPa)	Failure mode	Critical load (N)	Failure mode	Critical load (N)
A	162 ± 23	Detachment	45 ± 6	Detachment	44 ± 3
B	268 ± 91	Small spalls	25 ± 5	Small spalls	57 ± 8
C	135 ± 8	(None observed)	–	(None observed)	–
D	268 ± 26	Adhesion to stylus	55 ± 10	(None observed)	–
E	286 ± 51	Detachment	81 ± 9	Detachment	9 ± 2
		through-thickness cracking	38 ± 2	through-thickness cracking	44 ± 3

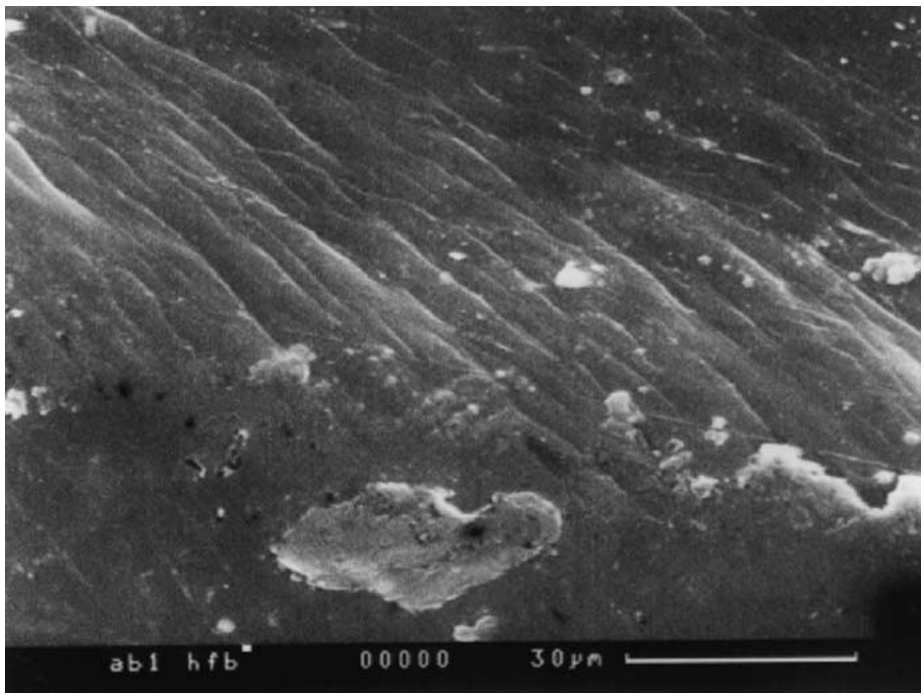

Figure 4 Gross plasticity at the edge of a scratch track made on a sample of coating E.

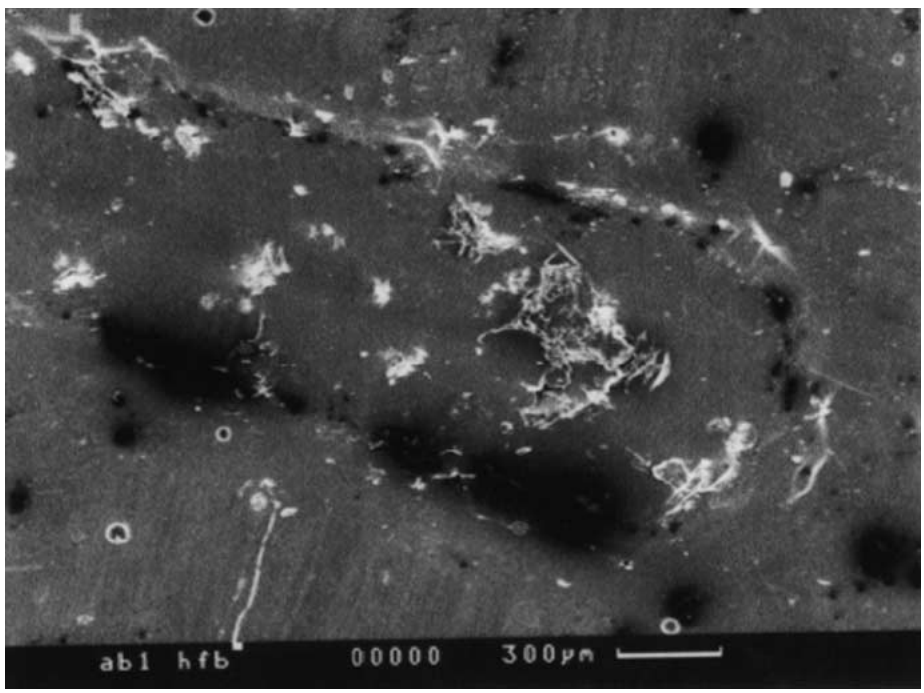

Figure 5 Shallow tearing at the terminal end of a scratch made on a sample of coating E.

and in the thickness values of the coatings made from them. No measurements were made of residual solvent contents at the end of the extended curing period at room temperature, but the scratch hardness values of coatings D and E were similar (Table II), as would be expected if the residual solvent contents were similar. Comparison of the scratch test behaviour of coatings D and E is therefore tentatively attributed to thickness differences. The thinner coating (E) showed two failure modes, through thickness cracking occurring first and then, at greater stylus loads, detachment (Table II). These kinds of failure were not observed with Coating D. Instead the only failure mechanism observed with Coating D was adhesion to the diamond stylus, which is not related to the test material being in the form of a coating: failure occurs completely within the composite with no apparent influence of the substrate-coating interface.

3.4. Effect of coating composition

In order to deduce the composition-related features in the scratch test with confidence it is necessary to compare samples all with the same thickness so that the influence of coating thickness can be disregarded. In the current work this restricts comparison to coatings A and E. It is noted that E is considerably harder than A. This may be a consequence of the plasticizing effect of the hydrocarbon present in coating A, which can be expected to affect properties in the cured resin as well as during coating preparation. The tendency to form through thickness cracks in E but not in A may also be related to the presence of plasticizer in A.

Scratch hardness should be unrelated to coating thickness provided the measurements are made using the part of the track prior to failure. Hence the scratch hardness results from Coatings A, B and C (given in Table II) can be used to deduce the effect of the presence of extender pigmentation. It is evident that the coatings with extender pigmentation (A and C) have much lower scratch hardness than unpigmented coatings (D and E) and the coating containing aluminium pigmentation (B). The scratch hardness of Coating B is similar to that of Coatings D and E, implying that the aluminium pigment is relatively inert, whereas in coatings A and C, presumably the deformability of the (mica) extender pigmentation and/or its poor adhesion to the polymer is responsible for the low hardness. This result was not anticipated, and requires further experimental investigation because, under certain conditions, aluminium flake is fairly ductile.

The thicker coatings, B, C and D showed no detachment nor through thickness cracking. In comparing Coatings B and D it is noted that the small spalls observed on B relate to failure within the coating and may in fact be closely related to the observation with D of removal of material that attaches to the stylus. Coating C did not show failure, as defined in this study.

It should be noted again that no measurements were made of the level of retained solvent in the coatings and that any differences in retained solvent between the different coatings would be expected to have a marked influence on the behaviour.

3.5. Coatings conditioned in sea water

Conditioning in seawater caused very large changes in behaviour in most cases and caused changes in the ranking of the different coatings (Table II). After hot seawater treatment, detachment of Coating E became very easy, with the critical load falling to a level that indicates the coating would be of no practical value in such an environment. The degradation was apparently primarily at the substrate-coating interface with Coating E since through thickness cracking was not observed until a much higher load was reached, similar to that required in the as-prepared coating. Coating B failed in a similar manner after hot seawater conditioning as in the as-prepared state, though required a much higher load. It is speculated that water caused plasticization and that the consequent increase in deformability led to an increase in the load that was required to cause spalling. The plasticization may have been a direct effect of water absorption within the polymer or an indirect effect due to de-bonding at the polymer-filler boundaries. Similarly, enhanced plasticization may have been the cause of the greater resistance to failure observed with Coating D after hot seawater treatment. As in the as-prepared state, hot seawater-treated C did not fail under scratch testing as conducted here.

4. Discussion

From studies of bulk polymers, Briscoe has deduced that the attack angle of the stylus has an important influence over the mechanism of deformation and fracture in a scratch test [19]. Under the conditions used here (stylus cone angle 120°/attack angle 30°), Briscoe showed that poly(methyl methacrylate) (PMMA) and ultra high molecular weight polyethylene (UHMWPE) respond entirely plastically. If the same behaviour were to be shown by the coatings, neither through thickness cracking nor coating detachment would occur. Therefore the dominance of through thickness cracking and detachment in the thinner coatings shows that the epoxy resin-based materials studied here were significantly more brittle than the thermoplastics studied by Briscoe. Although this is not particularly surprising, it does illustrate that the scratch test can discriminate successfully between coatings with different properties.

The scratch tests have made possible the discrimination between the different coatings studied here. Failure within the coating itself has been found to occur at higher loads in the presence of a plasticizing influence, whether in the form of a deformable additive (extender) or the absorption of water. Thin coatings (200 μm thick) were found to fail by detachment from the substrate or interfacial spalling. Treatment in hot seawater caused the interfacial adhesion to fall catastrophically in some coatings, but not in others. It is not known why this should be, though it is speculated that the hydrocarbon additive in Coating A acted as a barrier to water.

The thickness, composition, and the state of the coating (e.g., the level of absorbed water and/or retained solvent) all have an important influence on the scratch test behaviour. In this preliminary study it is impossible to interpret the results with certainty because of the restricted number of experiments and conditions explored

and the suggested explanations for the different observations must be regarded as tentative. It is nevertheless evident that systematic study of the effect of the various parameters would probably be most informative. This is particularly the case in determining the effect of pigments with different hardness and different adhesion to the matrix polymer. Such studies have not been carried out either on bulk composites or coatings. If augmented by observations to compare the mechanisms of failure in scratch tests conducted in the laboratory with those occurring in service failures would help establish the scratch test both as a predictor of service behaviour and as an aid to the identification of likely remedies for defective coatings.

5. Conclusions

Scratch testing is a promising tool for research into the fundamental failure mechanisms of polymer-based coatings and for ranking different coating compositions. Marine coatings have been found to become more resistant to failure when plasticized. Hot seawater treatment causes catastrophic reduction in strength of the interfacial adhesion with some coatings but others have been found to be much more resistant. More studies are required to determine the exact cause of this and to relate the observations to field performance. In particular, the exact dependence of scratch behaviour on coating composition should be examined in detail.

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