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Investigation of failure in paint films

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Direct "pull-off" tests have been carried out on mild steel plates coated with an "Alloprene"-based lacquer. Several unusual features were observed on the fracture surfaces, and attempts have been made to interpret these markings, and the implications of their origin on the test methods employed. Preliminary results led to an improved testing method but new markings were produced which have been interpreted, and appear to be caused by the interaction of periodic stress waves with the fracture. This technique has the advantages of reproducibility and simplicity.

1. Introduction

This paper considers tests carried out on a specific lacquer coating on a mild steel substrate. The object is to discuss the fracture markings observed on the surfaces of these specimens after they have been tested using a standard tensile testing procedure, and to interpret the markings. These interpretations may then be used as a basis for the modification and improvement of the test method. (All trade names will be defined in the Appendix).

2. Preliminary tests

2.1. Procedure

Many methods of testing paint films were reviewed [1–10] and each was found to have a varying number of advantages and disadvantages. The method finally adopted [3], the vertical "pull-off" test, was chosen for the following reasons:

(i) it appears to give reproducible results, which are relatively easy to interpret;

(ii) the equipment required is uncomplicated and readily available;

(iii) it is the test most frequently used in industrial laboratories.

A lacquer was prepared using 0.25 kg "Alloprene R20" dissolved in 0.25 kg Analar toluene, and plasticized using "Cereclor 42" in the ratio 70:30% w/w of "Alloprene" to "Cereclor". Sixteen mild steel "Pyrene" plates measuring 152 mm x 102 mm x 1.27 mm were prepared for coating by first degreasing them in a bath of boiling trichlorethylene, and then abrading them according to "British Standard" specifications. Finally they were washed in "Solveso" and dried in compressed air. They were coated as soon as possible after abrasion to prevent undue contamination of the surface.

A dry film thickness of approximately 75 μm was desired, as this is roughly the total film thickness of an industrial paint coating, so the plates were coated using a "draw-down" bar with an accurate clearance of 350 μm between the bar and the plate. They were then dried in air at 25° C for 24 h and in an oven at 40° C for a further 72 h. The film thickness on each plate was measured using a magnetic flux meter, after complete drying had occurred.

Each plate was then cut in half, and one 20 mm diameter aluminium "disc" was attached to each film surface using "Araldite" resin MY753 with hardener HY951. The plates were then put aside for a further 24 h at 25° C to allow the adhesive to cure.

Six specimens were tested in tension using an Instron testing machine, in order to find some measure of the force required to detach the film from the substrate. A cross-head speed of 5 mm min^{-1} was used, and the results were as follows:

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average dry film
thickness: $69 \pm 5\,\mu m$
mean nominal stress: $(5.88 \pm 0.73) \times 10^2 kN m^{-2}$.

The remaining specimens were tested using a bench-top "Elcometer" tensile testing device, which was employed simply to detach the film in order to study the types of failure occurring, and the possible weaknesses in the film.

An important part of any test is the identification of the site of initiation and subsequent path of failure, whether it is adhesive failure between the film and substrate, or cohesive failure within the film itself. The solutions to these problems are not always simple to obtain.

2.2. Observations

The first points to be noted from these preliminary tests were:

(i) that the stress at failure was much lower than the stress required to cause failure in an unsupported film of this formulation, in tension (up to $1.12 \times 10^4 kNm^{-2}$). This implies that either the film fails in the adhesive mode or the presence of the substrate produces a reduction in the tensile strength of the lacquer to a value below the strength of the adhesive interaction with the substrate;

(ii) that the surface markings on all the tested areas were very similar (Fig. 1);

(iii) that most of the specimens appear to have failed mainly in the adhesive mode.

The interpretation of the surface markings observed in these areas leads to an explanation of point (i), as follows:

(A) Each specimen contained an area of rib markings as shown in Fig. 1 and each one was in the same position on the tested area. These are caused by "stick-slip" propagation of the crack within the body of the film [11].

A propagating crack tends to accelerate as more energy becomes available through its propagation. It would be expected that this acceleration would continue until some specific terminal velocity had been reached, and the fracture would then continue at this maximum speed. However, the acceleration of the fracture front often appears to give rise to instability, and the most common example of this is crack forking, in which the fracture divides into two separate branches and is either halted, or slowed down, before one of the branches continues to propagate. This proces may occur many times, giving rise to a quasi-periodic effect.

Crack forking can only occur if the stress distribution at the fracture tip changes in such a way as to encourage propagation along two loci instead of the usual single axial direction (Fig. 2).

Under normal circumstances the stress distribution moves along with a propagating crack, so that the locus of maximum stress (b) coincides with the crack axis (Fig. 2), and this is the direction along which fracture will always occur. It is for this reason that a crack in a uniform field of force propagates in a straight line.

However, if the stress distribution at the propagating crack changes then the crack will follow one

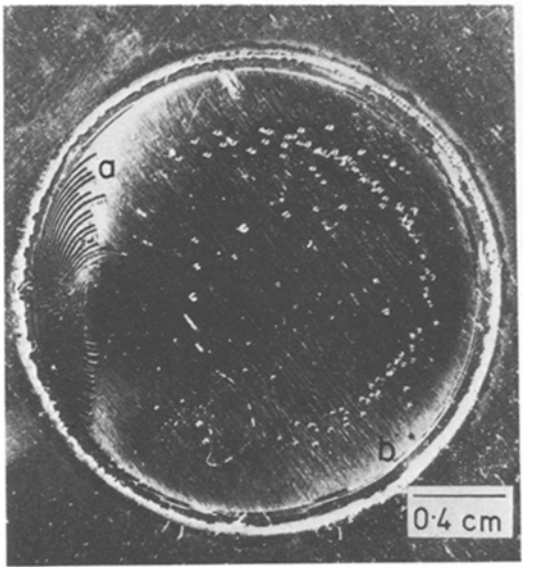

Figure 1 Typical example of a tested area. a, Rib markings; b, area of "adhesive" failure showing lumps of lacquer remaining on the surface.

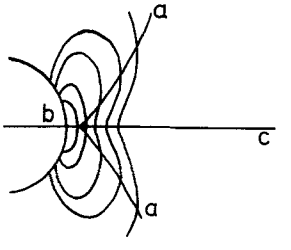

Figure 2 Stress distribution at a crack tip. a, loci of maximum stress; b, normal crack axis; c, normal path of fracture, [12].

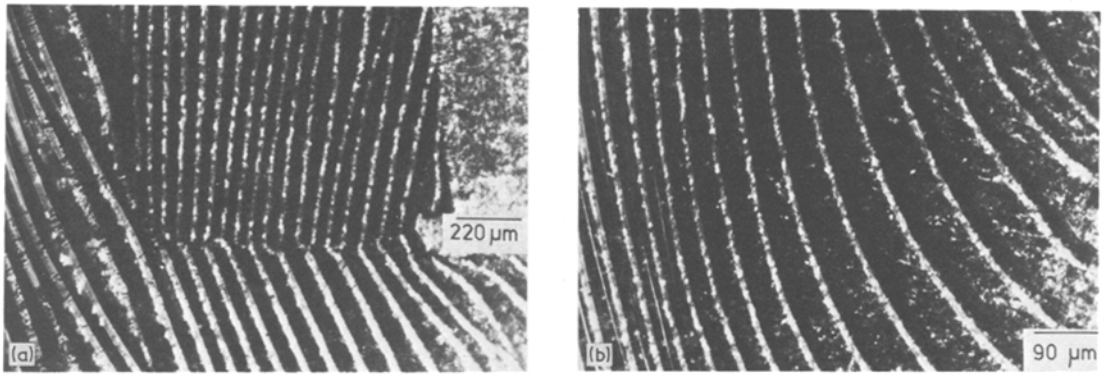

Figure 3 (a) Area of "stick-slip" fracture showing intersection of two fracture fronts. (b) Area of "stick-slip" fracture showing the typical curvature of the markings and their periodicity.

or both of the loci of maximum stress (a). This causes forking at the crack tip. As the crack grows in this way it will encounter lower and lower stresses, and will come to a halt unless the overall stress in the specimen is increased to compensate for this. When a high overall stress is achieved, the conditions maintaining the steady state are overcome, and as the stress in the test piece is far in excess of that necessary for propagation, a catastrophic phase of fracture will follow. The process occurs many times, and the "stick-slip" fracture is thus accounted for. Fig. 3a and b show typical areas of "stick-slip" fracture observed in the specimens, and as described by Andrews [11].

(B) The remaining area of each specimen was apparently a region of adhesive failure – the film appearing to have been completely removed from the substrate, leaving only occasional "lumps" of lacquer on the steel surface. However, on closer examination, using an optical microscope, these "lumps" were found to have a particular structure, and showed clear surface markings (Fig. 4).

This structure will be described as "nose-and-tail", and it was found that all the "noses" of the "lumps" pointed towards one particular area of the tested surface – this point was also the focus of the "stick-slip" markings. This is illustrated in Fig. 5. It was inferred that this was the point at which the initial failure occurred, and it is suggested that the surface features were formed in the following way (Fig. 6): assume that crack x is propagating at constant velocity at the interface between the lacquer and the substrate. Area y is an area of enhanced adhesion, for example where the lacquer is strongly keyed into the surface. When the crack reaches y those parts of it to the right and left of

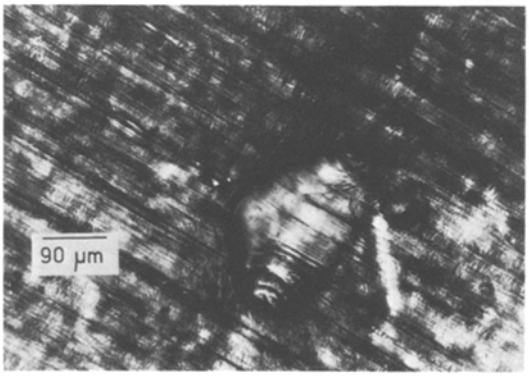

Figure 4 A typical example of an area of lacquer remaining on the substrate surface, showing the "nose-and-tail" structure.

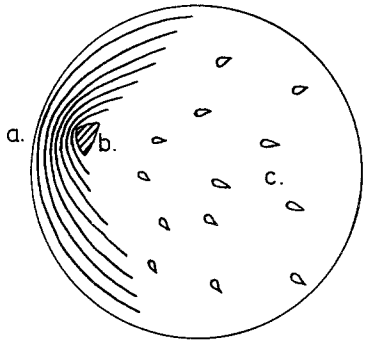

Figure 5 Diagram of a typical tested area. a, rib markings; b, focus of all fracture markings; c, exaggerated view of the pattern of the remaining lumps of lacquer.

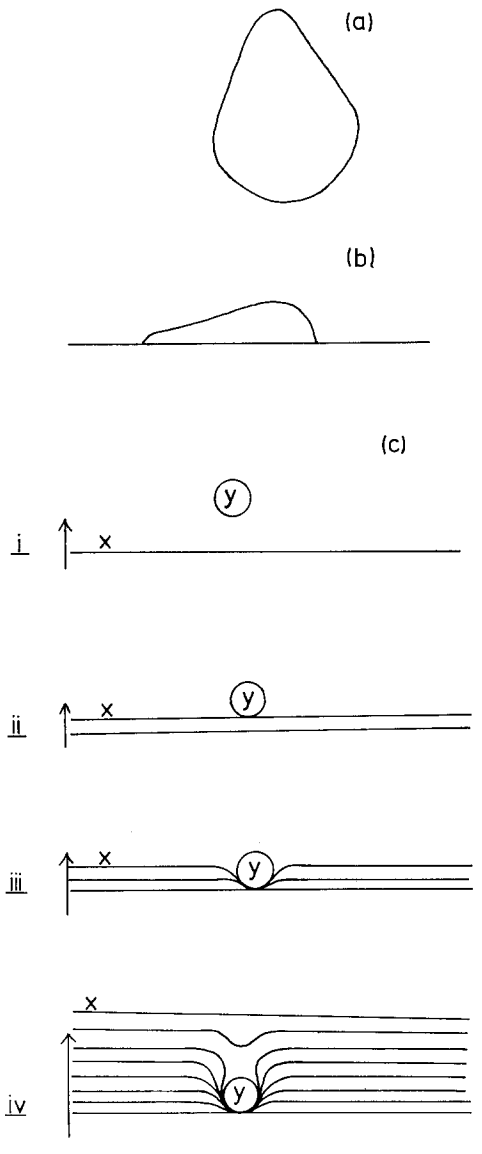

Figure 6 Typical shape of a remaining lump of lacquer (a) plan view. (b) Cross-section view. (c) Schematic representation of the process by which the lumps are formed.

this area continue to propagate, but the portion at y is held up, as the stress is insufficient to cause fracture here. As the crack moves further across the specimen the stress at y builds up until it is sufficiently high either to cause interfacial failure here or for the crack to climb through the film to a region of lower strength and move past the hold-up. It is the latter case which causes the "nose-and-tail" structure of the "lumps" because once the hindrance to crack propagation is by-passed, the crack front moves rapidly forward and down through the film to rejoin the main fracture front propagating at the weakest level in the film/substrate system.

Thus, the detailed markings on each surface may be examined using an optical microscope, and the point of initial failure deduced. Some effort was made using the optical microscope to identify the cause of the areas of increased adhesive strength – to detect some change in the structure of the interface – but no apparent causes could be found.

2.3. Discussion

In all cases the crack had initiated at a point 2 to 3 mm from the edge of the tested area, and the fracture front had expanded radially from this point. The mode of fracture must be related to the loading of the specimen, but the loading of the discs was intended to be symmetrical while the fracture pattern was non-symmetrical.

Dannenberg [6] found that a bubble with a low angle of advance tends to propagate by peel, while one with a high angle tends to move by the "stick-slip" mechanism. Fig. 7 shows an exaggerated view of uneven loading on a specimen, due to bending and inaccurate alignment. To the right-hand side the crack has a smaller angle of advance, and on the left-hand side a larger angle. Thus, the crack tends to propagate by a "peel-like" mechanism to the right, and "stick-slip" to the left. The sharper crack would tend to propagate more readily than the less sharp [14], which indicates that peel probably occurs before "stick-slip" failure. As this description coincides exactly with the markings observed on all the tested specimens it must be inferred that they are produced as a result of bending occurring within the system.

The important deductions to be made from these preliminary tests are:

(1) That a significant amount of bending occurs within the system, so the method of testing must be reviewed and suitably improved to eliminate this completely;

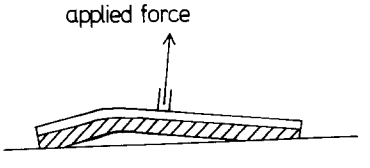

Figure 7 Exaggerated view of the effects of uneven loading on a specimen.

(2) that this bending probably causes a large increase in the stress at the point of initial failure, and hence premature failure of the specimen (which explains (i) above);

(3) that a more rigorous cleaning programme for the components in the system would not draw us too far from the types of surface encountered in industrial situations, but would reduce the number of random variables introduced into the properties of the interface.

Hence, an amended process for testing these films was developed.

3. Main tests

3.1. Procedure

The lacquer used in these tests was of exactly the same formulation as in previous tests, but instead of coating the whole steel plate individual discs were coated. Three 305 mm x 102 mm x 1.27 mm "Pyrene" plates were used, and these were first degreased in a bath of boiling trichlorethylene. Twenty 19.05 mm ($\frac{3}{4}$ in.) diameter discs were punched from each one using a fly-press with a die specially designed to prevent "dishing" of the discs, and produce as nearly flat discs as possible. The burrs were removed from the reverse side of the discs using emery paper, and a set of twenty was stuck in a double row along the centre of a glass plate using double-sided tape. These were abraded to the "British Standard" specifications and were immediately ultrasonically degreased for 5 min in boiling trichlorethylene. They were then washed in distilled water to remove any remaining surface deposits and finally in aceton to dry the surfaces. At all times the discs were handled with clean tweezers.

The discs were mounted in two rows on a cleaned steel plate as soon as they were dry and were coated using the 350 μm "draw-down" bar, in exactly the same way as before. They were allowed to dry on the base plate in air, but the surrounding film was cut away before they were put in the oven so that the elevation of the temperature would relax the strains thus introduced into the film. Three sets were prepared at two day intervals to allow for the bonding stage later on.

Instead of the original aluminium "dollies" mild steel cylinders were used this time, as they are more rigid than the aluminium, and their design means that they can be accurately aligned to prevent off-axis stress on the specimen. The dimensions of these "dollies" are given in Fig. 8,

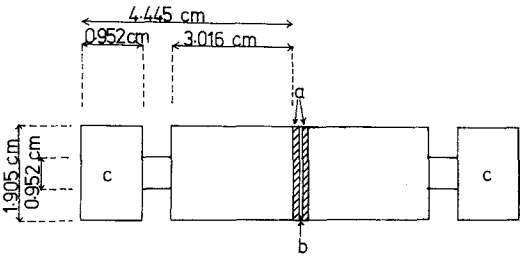

Figure 8 Preparation of a specimen for test. a, "Araldite"; b, steel disc with lacquer on one face; c, mild steel cylinders with dimensions shown.

and although the top surfaces were initially smooth they had to be lightly abraded to afford a suitable surface for the "Araldite" to key into.

Fifteen discs were selected from each set, avoiding any which contained obvious defects on the film; for example, bubbles or solid particles. Each disc was bonded between two cylinders as shown in Fig. 8, using "Araldite" as before, and all surfaces to be bonded were cleaned using methanol, as this is not a solvent for the lacquer. These specimens were then laid on specially designed alignment jigs and end-stops were screwed up to exert a force of approximately 5 kg along the axis of each cylinder.

The specimens remained in the jigs for 48 h to ensure accurate alignment, total curing of the adhesive and to give a uniform thickness of "Araldite" in each joint. French chalk was spread lightly over the jig to reduce friction and to prevent any excess "Araldite", which may be squeezed from the joints from bonding the samples to the jig.

This was repeated with each set of discs, although the third set was stored in darkness, but in air, for 2 months in order to investigate the effects of the extended drying time.

Two sets of clamps were specially designed for the Instron to hold the specimens firmly and prevent any movement of the test-pieces away from the stress axis. Once more a cross-head speed of 5 mm min^{-1} was used for the test, and a rapid chart speed was used to record any changes in the stress/strain curve.

The results obtained from these tests were as follows:

Set	Film thickness (μm)	Drying time	Force to cause failure (kN m^{-2})
1	125 ± 2.0	5 days	(5.20 ± 0.66) × 10^3
2	200 ∓ 11.4	5 days	(4.28 ± 0.26) × 10^3
3	215 ± 10.1	2 months	(9.54 ± 0.85) × 10^3

Comparing sets 1 and 2 the well recognized effect of film thickness variation can be observed; the thicker film requires a lower force to cause failure. However, comparing sets 2 and 3 illustrates the effect of the longer drying time, the force to cause failure in set 3 is over twice that required to cause failure in set 2.

It is clear from the observations made of the fractured surfaces that many of the problems encountered in the preliminary tests, and outlined in Section 2.3, have now been eliminated, and greater film strengths are measured when the applied stress is perpendicular to the plane of the film.

3.2. Observations

No consistent trend was observed in the types of markings occurring on the fracture surfaces, as there had been in previous tests, and there was no indication that there was any deviation from stress in a direction perpendicular to the plane of the speciment. However, in the regions where cohesive breakdown had occurred, markings similar to those in Fig. 9 were observed. It is suggested that these markings are produced by a similar mechanism to "Wallner" lines, and a useful account of this is given in Andrews [13]. This is considered under three headings

3.2.1. Propagation of fracture

It is suggested that the crack propagates more rapidly than the rate at which the Instron jaws are separating, therefore it will move in short jumps. The crack will move until there is insufficient energy available for its continued propagation, it will then remain stationary until the stress has built up sufficiently to propagate the failure further.

3.2.2. Origin of stress waves

A stress wave is generated at the point of fracture by a sudden release of energy as the crack begins to propagate. As the stress on a stationary crack builds up it has to reach some excess over the stress necessary for continuous propagation – there is thus an energy barrier. Once this level is reached and the crack begins to move there is an energy excess, and the stress wave is produced by the sudden release of elastic energy.

3.2.3. Interaction of fracture front and stress wave

This stress wave travels faster than the fracture, and may be reflected at the surfaces of the specimen, causing it eventually to meet the fracture front. According to the direction of approach of the stress waves they will momentarily both magnify and distort the stress distribution at the fracture front, with a possible deviation of the front from its original direction. This causes grooves or pits in the fracture surface (Figs. 9 and 10). Sometimes this deviation is periodic because a train of regularly spaced stress pulses interact with the travelling fracture. These pulses could be caused by the propagation of the fracture, as described above.

The markings observed can be shown to occur at the intersections of two circular wave patterns, probably the first reflected stress wave from the top surface and the first from the bottom surface, as described in Fig. 11.

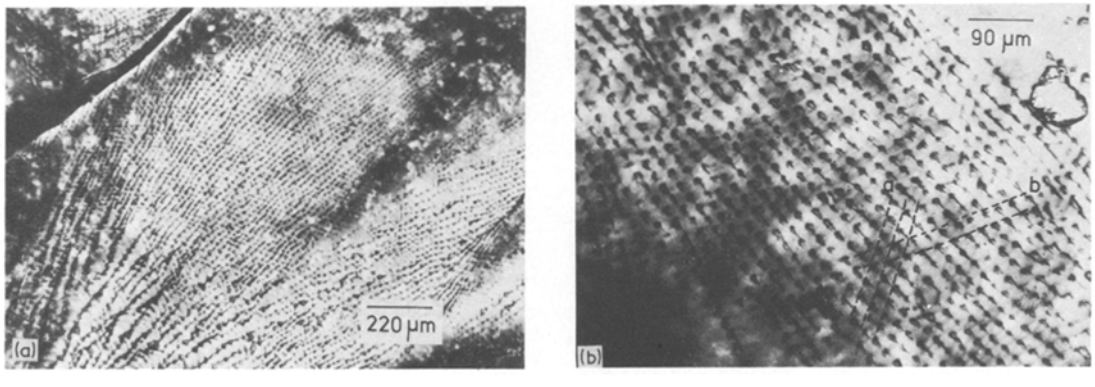

Figure 9 (a) Markings observed in areas of cohesive failure. (b) Markings observed in areas of cohesive failure showing periodicity in two directions, illustrated by lines a and b superimposed on the photograph.

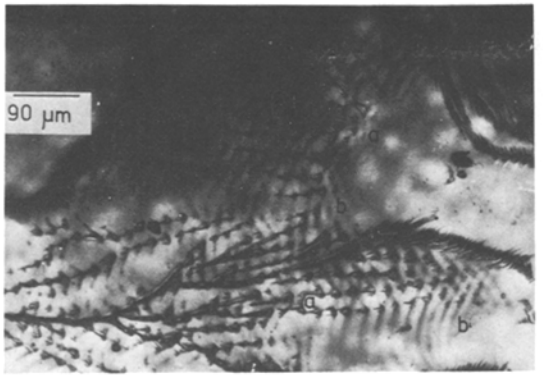

Figure 10 Points of intersection of stress waves can be clearly observed, a. Conventional Wallner markings appear in areas, b.

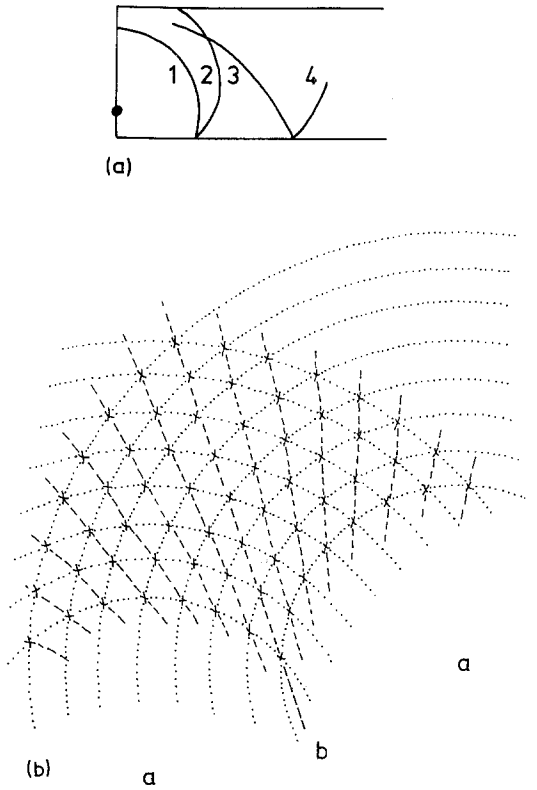

Figure 11 (a) Reflection of stress waves. (1) System concentric with fracture front. (2) First reflection from upper surface of specimen. (3) First reflection from lower surface. (4) Second reflection from upper surface [13]. (b) Schematic representation of the formation of the observed markings (a) Foci of periodic stress waves (. . . .) (b) Focus of surface markings (–x–x–). (Representation first suggested by Keith Reading while a member of the "Interfaces" group in Oxford).

3.3. Discussion

As the second method of specimen preparation appeared to be suitable, it was adopted for all further tests. A minor change was made. The face of the "dolly" attached to the reverse surface of the disc now has a series of V-shaped circular grooves 0.127 mm deep machined into the surface to afford a more suitable surface for the "Araldite" to key into.

In all subsequent tests similar markings to those described above were observed.

4. Conclusions

Simple "pull-off" tests were carried out on mild steel plates coated with an "Alloprene"-based lacquer. The surface features observed on the fractured specimens were interpreted and the site and cause of failure in each specimen was deduced. An improved test method was devised as a result of these deductions, and new markings were observed, which have also been interpreted. This technique has been adopted as the standard test method as it is simple to carry out and gives reproducible results.

Appendix

Alloprene R20, chlorinated *cis*-polyisoprene: ICI Ltd, Mond Division.

Cereclor 42, a chlorinated paraffin: ICI Ltd, Mond Division.

Pyrene, manufactured mild steel plates.

Solveso, solvent cleaner: ICI Ltd, Mond Division.

Araldite, epoxy resin and hardener: Ciba-Geigy (UK) Ltd.

Elcometer, bench-top tensile testing device: Elcometer Ltd.

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