Chapter 6

Fouling on Paints Containing Copper and Zinc

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6.1 INTRODUCTION

Fouling on ships causes hull roughness leading to increased frictional resistance and an increase in fuel consumption if the service speed of a vessel is to be maintained. Removal of fouling necessitates expensive dry-docking and therefore periods out of service. Self-polishing copolymer (SPC) antifouling paints control most animal and weed fouling, but the slime-forming organisms, notably bacteria and diatoms, persist. In SPC systems, triorganotins are a major toxic component polymerised with unsaturated monomers to produce film-forming polymers with a high concentration of organotin groups. Other toxic components may include cuprous oxide and sometimes a small amount of zinc oxide. SPC paints hydrolyse and dissolve in seawater releasing the biocides at a controlled rate during service. Polymer dissolution takes place at a higher rate where there is greater turbulence, e.g. in areas of hull roughness, and erosion of the coating is faster in these areas resulting in a progressive polishing of the hull surface with time.

Cuprous and zinc oxides were compared as additional biocides in a SPC paint, i.e the antifouling performance of different combinations of cuprous and zinc oxides in such paint was tested.

Fouling organisms found on the zinc- and copper-containing SPC paints were compared with those on non-toxic panels to determine the selective action of the biocides on the local population of fouling organisms. In addition, a comparison was made of the relative influences of seasonal variation and extended periods of exposure on fouling levels on the test paints.

6.2 MATERIALS AND METHODS

The antifouling efficiency of cuprous and zinc oxides was evaluated by exposing test panels coated with SPC antifouling paint incorporating these biocides on experimental rafts. Two raft trials were run concurrently over a period of fifteen months (August 1982-November 1983) to test five paints all based on the tributyltin methacrylate / methyl methacrylate SPC system (Table 1). Cuprous oxide and zinc oxide were used singly and in two different combinations and non-toxic calcium sulphate was used as a substitute in a control paint. Two coats of each test paint were applied by weight to $100cm^2$ Formica panels to achieve a dry-film thickness of $100\mu m$.

The panels were attached in groups of twenty five to both sides of wooden plates, which were vertically suspended to a depth of 1.5m from a raft in the Yealm estuary, Newton Ferrers, Devon. In order to remove any variation that may occur due to the position of the panels on the raft, the arrangement and sampling of the wooden plates was randomised. They were placed 0.8m apart on the central area of the raft to avoid any currents or turbulence near the edges. It was assumed that any variation caused by panel position on the wooden plates would be mainly the result of differences in

TABLE 6.1

Composition of self-polishing copolymer test paints

Paint	Components
A	tributyltin + cuprous oxide
B	tributyltin + zinc oxide
C	tributyltin + calcium sulphate
D	tributyltin + cuprous oxide + zinc oxide 2 : 1
E	tributyltin + cuprous oxide + zinc oxide 1 : 2

The pigments cuprous oxide, zinc oxide and calcium sulphate were present at approx. 50% weight, and tributyltin was included at approx. 30% weight.

depth (irradiance level) rather than horizontal position. A randomised block design was used for the arrangement of the panels on the wooden plates. There were five replicates of each test paint on one side of a plate with one replicate at each depth.

6.2.1 Raft trial 1

Three hundred and seventy five panels were immersed in August 1982. Five replicates of each paint (i.e. one side of a wooden plate) were randomly sampled at monthly intervals following increasing exposure periods up to fifteen months. Each successive set had been exposed for one month longer than the previous set. This trial tested variation in fouling between the test paints and the pattern of fouling over increasing exposure periods.

6.2.2 Raft trial 2

Five replicate panels of each paint were immersed monthly and removed after three months exposure. These monthly immersions were continued for twelve months (August 1982-July 1983). Three hundred panels were exposed in all. This trial tested variation in fouling between the test paints and seasonal fouling variation.

A plate of non-toxic, uncoated, black Formica panels was also immersed. There was one panel for every twenty five test panels sampled, immersed at the same time and for the same period as the test panels.

6.2.3 Assessment of fouling on exposed panels

Fouled panels were examined visually and microscopically to determine the main organisms present and the percentage of the panel surface covered by these organisms. Fouling was then measured by chlorophyll a concentration and dry weight throughout both trials and ashed weight was also measured for panels sampled on February 22nd 1983 and thereafter. Panel surfaces were divided into five strips. Two strips per panel were used for chlorophyll determination and a further two strips were used for dry and ashed weight determinations. Total fouling levels for each panel were calculated from measurement of these strips.

Fouling material was removed from the panel surface using cotton wool buds and suspended in filtered seawater (Whatman GF/A). The suspension was centrifuged at 1500g in a Beckman T-J6 centrifuge for 10min and the supernatant discarded. Successive extractions in dimethyl sulphoxide were carried out following the method of Shoaf and Lium (1976) and the chlorophyll a concentration determined spectrophotometrically using the equation:

$$[\text{chlorophyll a g m}^{-3}] = 11.47\ A664 - 0.4\ A630 \quad \text{(Holden, 1976)} \qquad (1)$$

where A664 and A630 are absorbances at 664nm and 630nm respectively. For dry weight determination, the pellet of fouling material was obtained as above and then washed three times in distilled water to remove salts. These crystallise out on drying the sample and interfere with weight measurements. The samples were transferred to tared porcelain crucibles and dried to constant weight at 80°C. They were than placed in a furnace at 400°C for 16h after which they were removed to a desiccator until cool and the ashed weights measured.

Temperature, pH and salinity were monitored throughout the exposure period of both trials.

6.3 RESULTS

During the raft trials, a study was made of the selective action of copper and zinc on the seasonal populations of fouling diatoms. The results of the visual and microscopic examination of the fouling organisms on both the non-toxic, uncoated panels and the five SPC test paints were very similar in the two raft trials, so the data for trial 1 are presented here (Figs 6.1-6) and any differences recorded for trial 2 will be indicated. A much wider range of algal species was found on paint C, where tributyltin was the only biocide, than on those paints containing cuprous and/or zinc oxide. Several species of macroalgae were found on paint C, together with a greater number of diatom species, and hydroids were also present. The filamentous green alga Ulothrix was found on paint C between May and August. It was also found on paints B, D and E, but was absent on paint A. Enteromorpha was found on paint C between May and December and also on paints B, D and E between July and December, but again it was not found on paint A. The diatoms Achnanthes longipes and Achnanthes subsessilis were found on paint C, but not on any of the copper- or zinc-containing paints (A, B, D or E). In addition to Enteromorpha and Ulothrix, Ectocarpus was found on paint B. Amphiprora hyalina was the predominant diatom for most of the year on all the cuprous and zinc oxide-containing paints. On paint C, this species was only found during January to February and between September and October. Stauroneis amphoroides was also found on all five test paints for most of the year. Amphora coffeaeformis was again found on all five test paints and like A. hyalina, it was present in lower numbers and for a more limited period on paint C. Amphora veneta was found on paints A and C between September and October, on paint B in February and on paints D and E in July and October. A. exigua

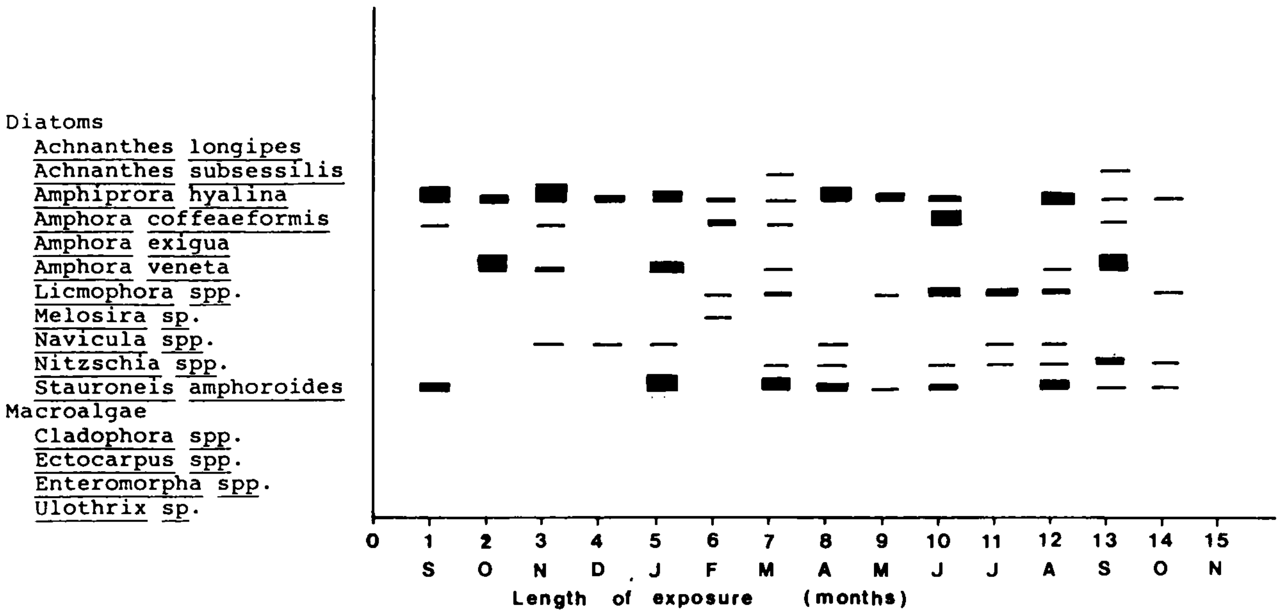


Fig. 6.1. Speciation and percentage of the panel surface covered by fouling organisms on SPC test paint A in raft trial 1. Bars represent the mean visual estimation of five replicate panels at each exposure time.

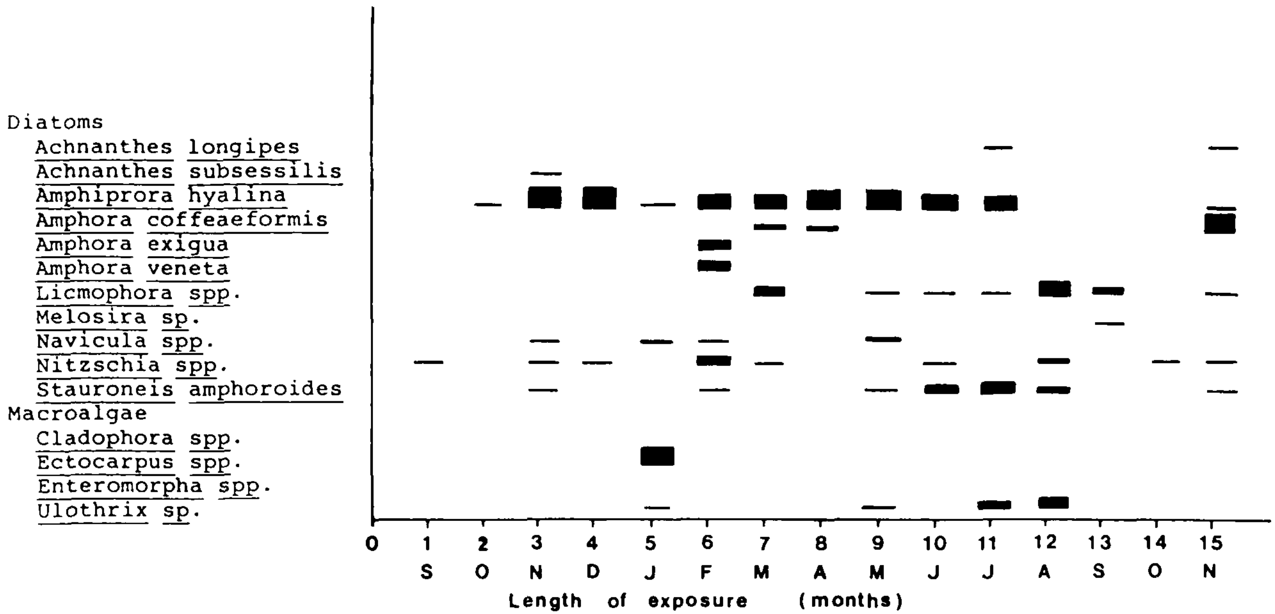


Fig. 6.2. Speciation and percentage of the panel surface covered by fouling organisms on SPC test paint B in raft trial 1. Bars represent the mean visual estimation of five replicate panels at each exposure time.

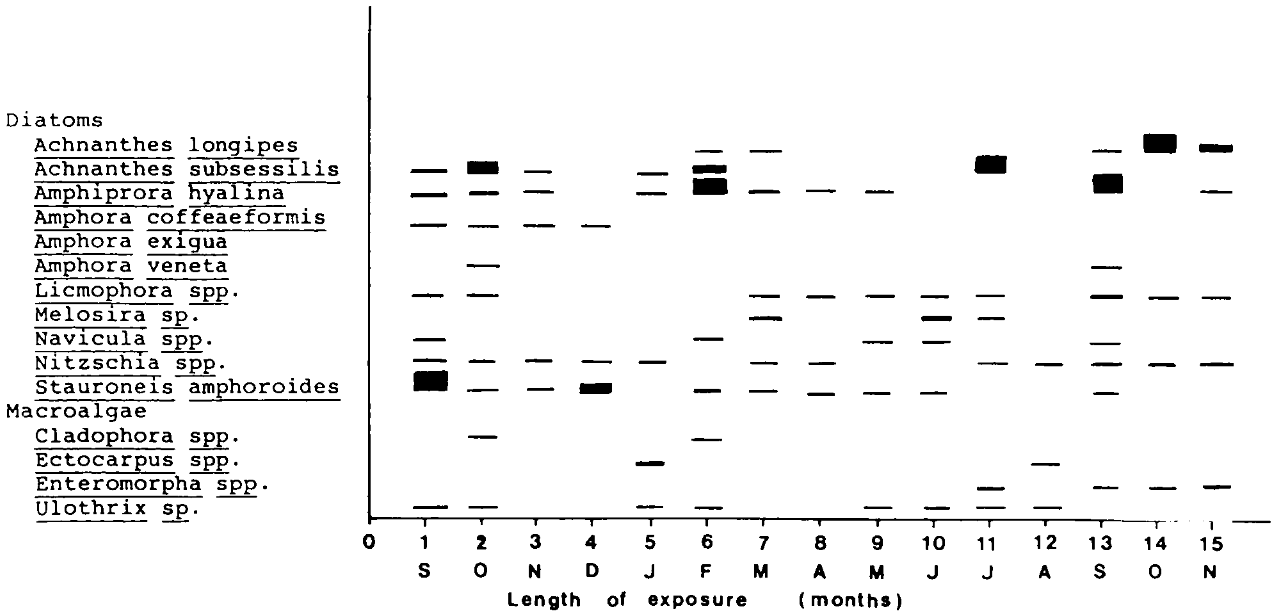


Fig. 6.3. Speciation and percentage of the panel surface covered by fouling organisms on SPC test paint C in raft trial 1. Bars represent the mean visual estimation of five replicate panels at each exposure time.

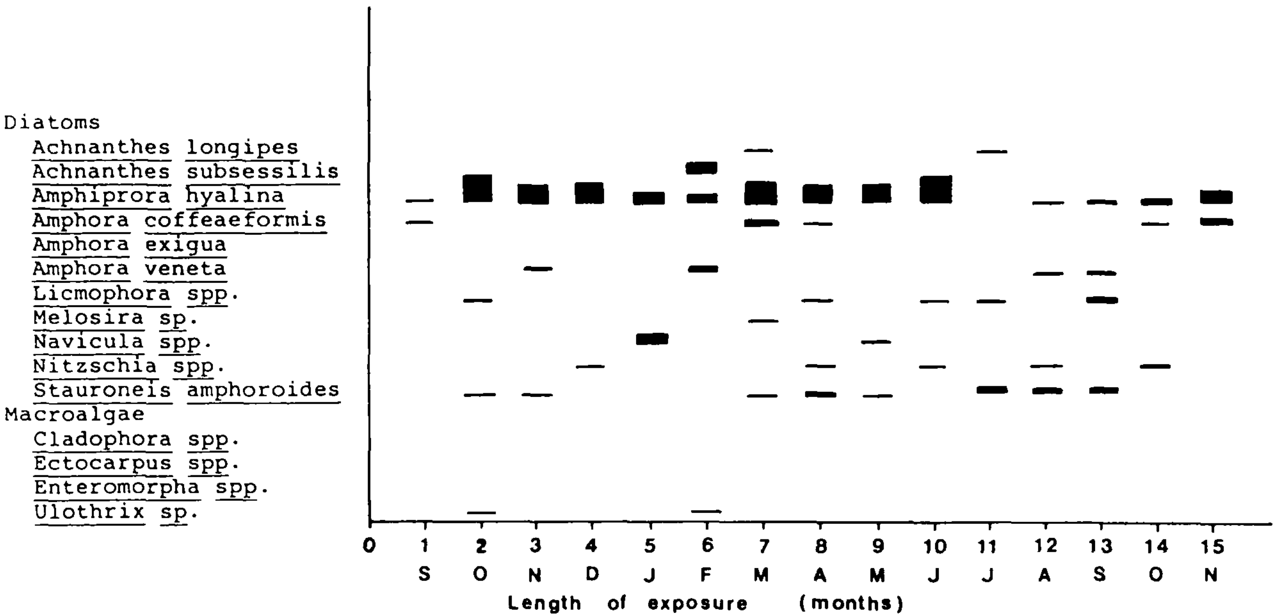


Fig. 6.4. Speciation and percentage of the panel surface covered by fouling organisms on SPC test paint D in raft trial 1. Bars represent the mean visual estimation of five replicate panels at each exposure time.

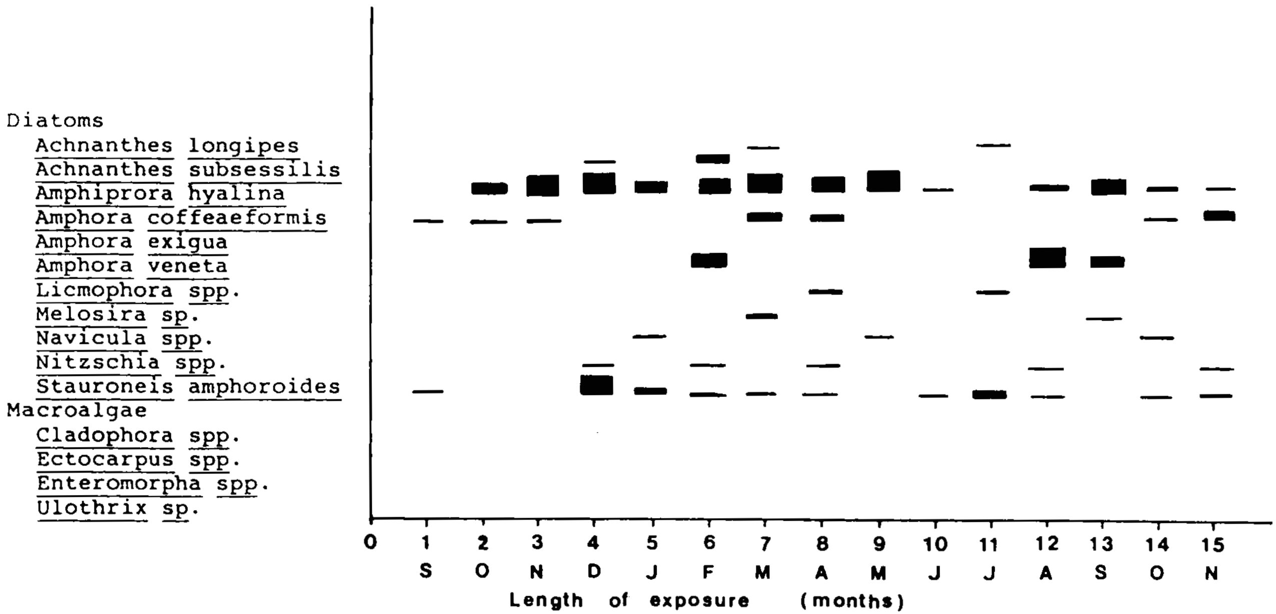


Fig. 6.5. Speciation and percentage of the panel surface covered by fouling organisms on SPC test paint E in raft trial 1. Bars represent the mean visual estimation of five replicate panels at each exposure time.

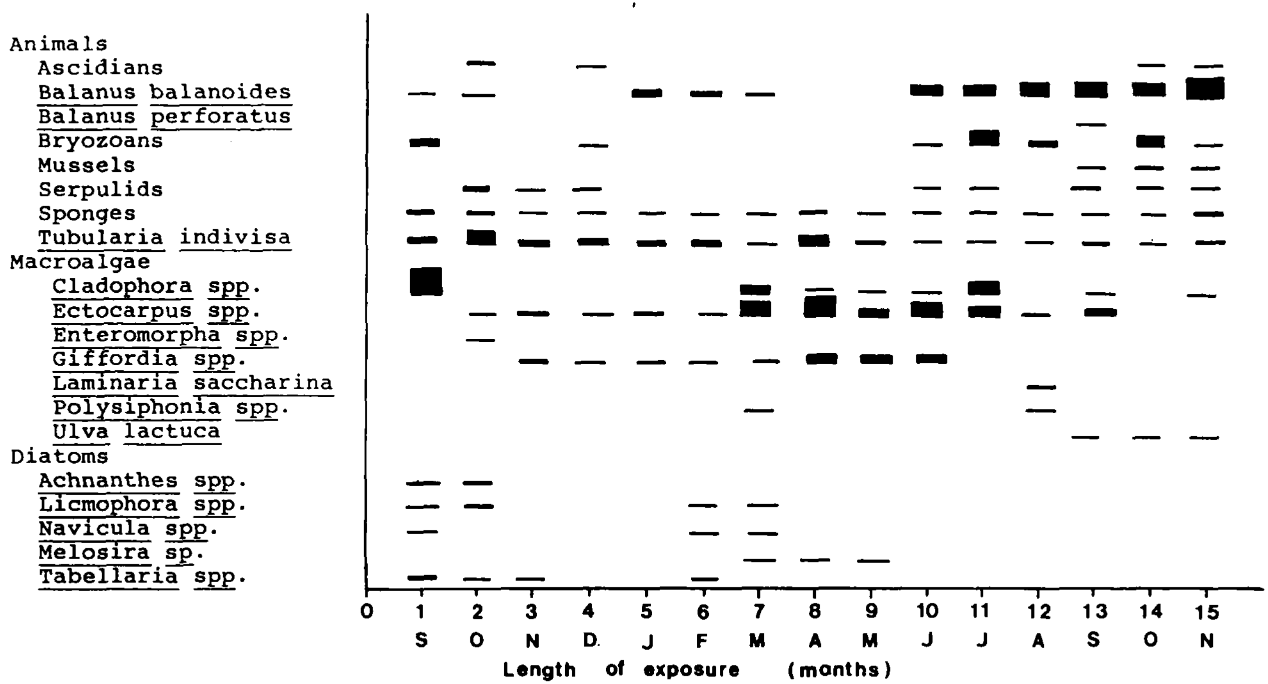


Fig. 6.6. Speciation and percentage of the panel surface covered by fouling organisms on uncoated, non-toxic Formica panels in raft trial 1. Bars represent the visual estimation of one panel at each exposure time.

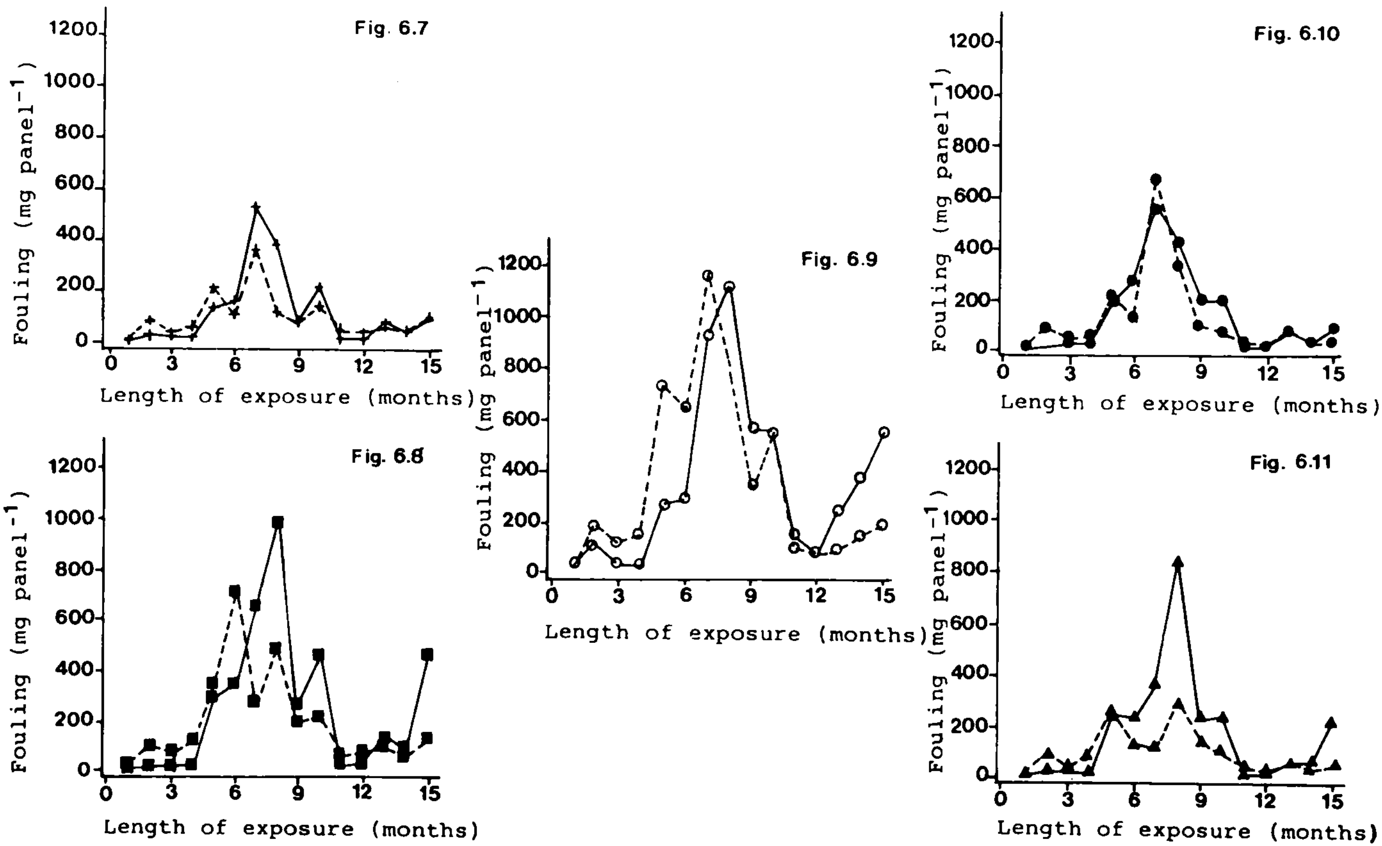
was found on paints B, D and E. Licmophora species were found on all the test paints for a large part of the year, but in relatively low numbers. Other commonly found species were of the genera Nitzschia and Navicula.

Non-toxic uncoated panels were more heavily fouled than the test paints and also were fouled by a more diverse range of organisms. This included extensive fouling by macroalgae from February until August with highest algal fouling in June and July mainly of Ectocarpus and Giffordia species. During the period September to February, there was very little algal fouling on the panels, but Ectocarpus and Enteromorpha were present. In March to May, Cladophora species were found together with Ectocarpus and a little Polysiphonia. They provided a thin algal covering over about 80% of the panel surface. Ulva lactuca was found in both trials in September to November, but Laminaria saccharina was found only in trial 1, in August. From August onwards the algal cover became reduced and animal fouling increased. Diatoms were mainly epiphytic on the macroalgae and were therefore present in highest numbers during the summer. They included Tabellaria, Licmophora, Navicula, Achnanthes and Melosira species. Heavy silt deposits were found on the non-toxic uncoated panels throughout the year and this was the major constituent on these panels during the winter. Animal fouling occurred mainly during June to November and consisted of hydroids, barnacles, serpulids and bryozoan colonies. Hydroids, mainly Tubularia indivisa, were found throughout the year, the dead stalks persisting after the colonies had developed. The barnacles were mainly Balanus balanoides, although one specimen of Balanus perforatus was found following thirteen months exposure in trial 1. High numbers of large barnacles were found in June to November following ten to fifteen months exposure (trial 1), while they were present in much lower numbers over this period on those panels exposed for three months (trial 2). Barnacles covered 50-80% of the surface of panels in trial 1 during September to November. A high proportion of the serpulid worms were Spirorbis species and non-toxic panels of trial 1 continued to show the broken calcareous serpulid tubes until December, although none were found in trial 2 after September. Large bryozoan colonies were also found in trial 1 in June to November, covering up to 40% of the panel surface and often covering silt, barnacles and other fouling organisms. Only occasional small colonies of bryozoans were found on non-toxic panels of trial 2 exposed for three month periods.

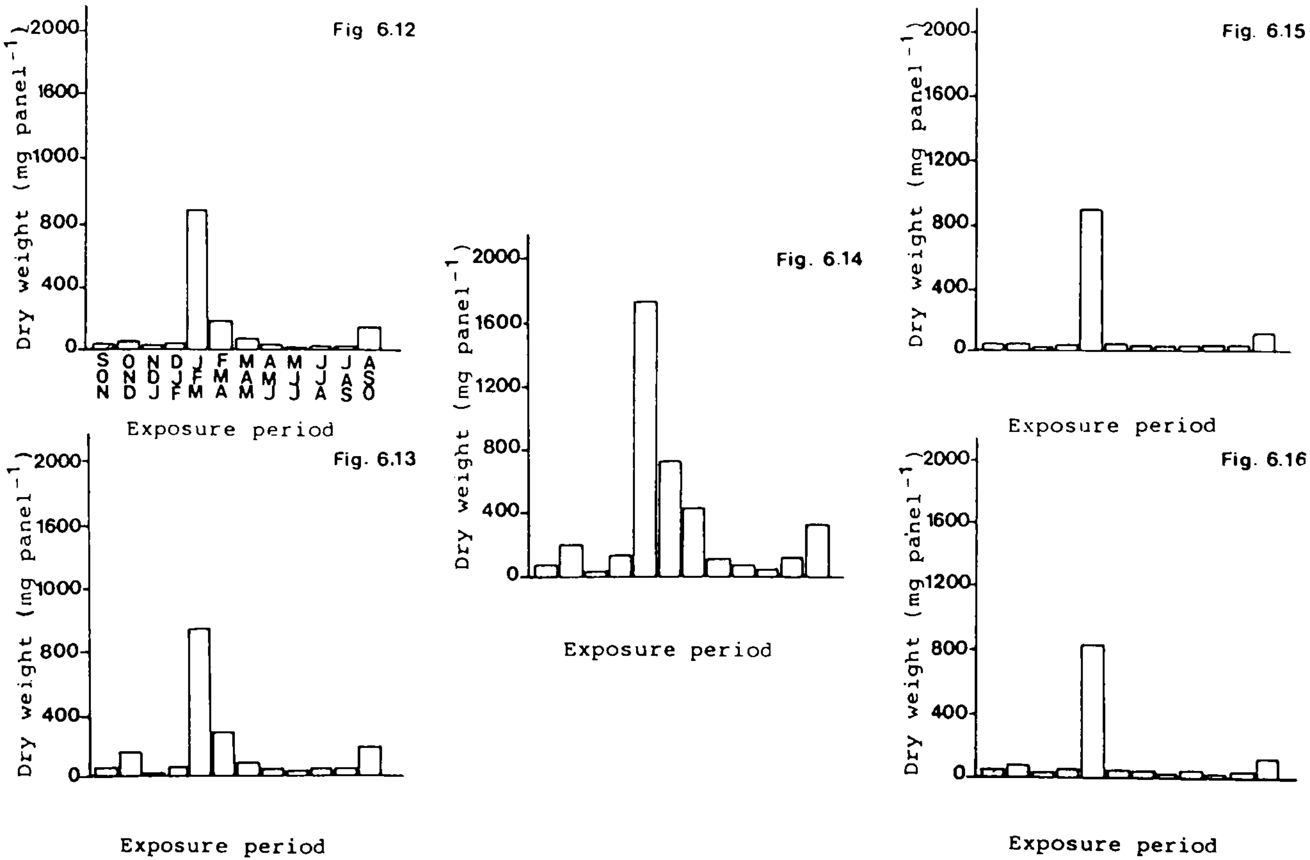
Large numbers of a variety of sponge species were found on the non-toxic uncoated panels throughout the year and shellfish were occasionally found. Ascidians were also found during the summer.

The variables used to assess fouling levels on exposed raft panels (chlorophyll a concentration, dry weight and ashed weight) were found to show high and significant correlation, at the 95% confidence level, for most of the exposure periods of both trials (Figs 7-16), i.e. from February 1983- November 1983 in raft trial 1 and from the fourth three month exposure period (December 1982) in trial 2 until the end of the trial. All the test paints follow a similar fouling pattern in both trials. The figures show a large peak of fouling in January to May with a smaller peak in August to November. A small peak was also found in June and in trial 1, another small peak occurred in December to February. The fouling levels on each test paint were found to vary significantly, at the 95% confidence level, with the final month of exposure (trial 1) and with the month of immersion (trial 2). In trial 1, where the panels were exposed for increasing periods up to fifteen months, it appears from the figures that the significant fouling variation which occurs with time is due to seasonal variation and not to increasing exposure time of the test paints. This was confirmed by the results of trial 2, where the panels were exposed for a constant period of three months with immersions throughout the year. It is apparent that the time of year that the test panels were immersed had a greater effect on fouling levels than the total length of the exposure period.

Differences in fouling between the test paints and between the five depths of panel immersion, corresponding to the five vertical positions on the wooden plates, were considered in a two-way analysis of variance test on the ln transformed data for each exposure period, i.e. for each month in trial 1 and for each three month period in trial 2 (see French, 1985 for tables of data and statistical analysis). Since seasonal variation in fouling was greater than that between the test paints, the entire fifteen month exposure period could not be considered. For those sample times where the test paints were found to have significantly different fouling levels at the 95% confidence level, t-tests were used to compare individual paints. From these a general ranking order relating to antifouling performance emerged. Paints A, D and E had the lowest fouling levels and the relative order of their antifouling activity varied with the particular fouling variable



Figs 6.7-11. Fouling on the SPC test paints A (+), B (■), C (o), D (●) and E (▲) in raft trial 1. Chlorophyll a x 10^{-3} (——) and dry weight (- - -). Points are means of five replicate panels.



Figs 6.12-16. Fouling on the SPC test paints (A, B, C, D and E respectively) in raft trial 2 estimated by dry weight. Bars represent the mean dry weight of five replicate panels.

and with the exposure period considered. Significant differences, at the 95% confidence level, between these three paints were rarely found. Paints B and C both had significantly higher fouling levels, within 95% confidence limits, than paints A, D and E and paint C was often found to be significantly more fouled than paint B, at the 95% confidence level. To test the ranking order of paints indicated by t-tests for each sample time over the entire exposure period of each trial, a weighted mean for each test paint was calculated and these are shown in Table 2 for raft trial 2. Taking each variable in turn viz. chlorophyll a concentration, dry weight and ashed weight, the fouling means of each paint for each month in trial 1 and for each three month exposure period in trial 2 were then compared to the corresponding weighted means by computation of the correlation coefficient by a least squares regression. The three variables generally showed high and significant correlation, at the 95% confidence level, between the fouling means for each sample time and the ranking order of paints given by the weighted means. It can be seen from Table 2 that the three variables do not indicate the same order of ranking for paints A, D and E, but the overall impression gained is very similar to that formed from t-tests. Therefore in both trials, the overall trend was that there was very little difference in the antifouling performance of paints A, D and E. Paint C, the control paint, had poor antifouling activity compared to these three paints and paint B had intermediate antifouling activity.

TABLE 6.2

Weighted means for the SPC test paints in raft trial 2

Paint	Chlorophyll a content	Dry weight	Ashed weight
A	2.827	4.128	3.029
B	3.827	5.652	3.671
C	5.024	6.269	4.876
D	2.614	4.104	2.986
E	2.955	4.085	2.805

Depth was also considered as an influence on fouling levels on the test paints. Fouling variation with depth was found to be significant, within 95% confidence limits, for some months in trial 1 and for some three month exposure periods in trial 2. This was the case, for example, for 5 months out of 15 for fouling levels estimated by dry weight in trial 1. However no consistent pattern of fouling variation with depth was found, although in trial 2, panels exposed between 1.3 and 1.5m did show heavier fouling more often than those between 1.0 and 1.3m.

6.4 DISCUSSION

Raft trials are a good method of testing a large number of formulations with replication. They are rigorous tests of antifouling activity as they are performed at sites rich in fouling organisms similar to the situation of a ship in harbour which is where most fouling occurs. No anticorrosive coating was used on the Formica panels as would be the case on a ship in service, because there is some evidence that the type of anticorrosive may affect the amount of fouling or the speciation of organisms that develop (C. Anderson, personal communication, 1985; Robinson et al., 1985). Electron microscopy has shown that anticorrosives retard the polishing rate of SPC paints and this may influence the antifouling performance.

Comparison between non-toxic, uncoated panels and panels coated with the SPC test paints exposed for the same period illustrated the effectiveness of the antifouling biocides tested. The biocide-containing SPC paints had considerably reduced total fouling levels compared to the non-toxic panels and the speciation of fouling organisms was also restricted. The selective action of particular biocides could also be seen in the variation of species, in particular of diatoms, on the test paints. All five SPC test paints contain tributyltin, so all the organisms encountered must possess some resistance to this biocide. In the presence of tributyltin only as in paint C, animal fouling was prevented with the exception of the hydroid *Tubularia indivisa*. Macroalgal fouling was also reduced compared to the non-toxic panels and was restricted to relatively few resistant species. On paint B, with zinc oxide in addition to tributyltin, no animal fouling was found and macroalgal fouling was further restricted. *Ulothrix*, *Enteromorpha* and *Ectocarpus* occurred on the control paint C and on paint B, but were absent when copper was present instead of zinc (paint A). Taylor and Evans (1976) and Millner and Evans (1980) have previously shown Ulothrix to be resistant to organotin paints and this is confirmed in these trials. It must also have some tolerence of zinc oxide. Enteromorpha has been found to be more sensitive to organotins than Ulothrix (Millner and Evans, 1980), but it was found on all the SPC test paints except paint A, which suggests that it has some resistance to all three biocides. Ectocarpus has been found to be resistant to organotins (Millner and Evans, 1980) and has also been found to develop resistance to heavy metals (Clitheroe and Evans, 1975). In this study Ectocarpus was found only on paint B indicating tolerance to tributyltin and zinc oxide. Its absence on paint C suggests that it does not compete successfully with Enteromorpha and Ulothrix when tributyltin is the only biocide present. The use of zinc and/or cuprous oxide in paints A, B, D and E resulted in a smaller range of diatom species. Only those able to compete successfully under the selective pressure of these metal oxides and tributyltin were able to grow in the slime-film. Achnanthes subsessilis and Achnanthes longipes were found only on paint C, indicating that these diatom species are tolerant to tributyltin but not to copper or zinc. This is contrary to the findings of Hendey (1951) who found that both these species and particularly A. longipes showed resistance to copper-containing paints. However, Callow et al. (1976) found that Achnanthes species could form up to 80% of the fouling organisms following 20 weeks exposure of paints coated with an organotin antifouling paint and both these species were found on paints with tributyltin as the only biocide at various sites around the world by Callow (1986). Amphiprora hyalina and Stauroneis amphoroides were the predominant diatoms on the five test paints. They appear to be able to compete successfully under the influence of all three biocides. Hendey (1951) and Harris (1946) found A. hyalina to be strongly resistant to copper-containing paints and Callow (1986) found Amphiprora species on a copper- and tributyltin-containing paint exposed on the east coast of England. Stauroneis has also been found in large numbers on a tributyltin paint (Blunn, 1982) and this diatom has been found to be resistant to both copper and tributyltin at several sites around the world (Callow, 1986). Various species of the genus Amphora were found on the SPC test paints. A. coffeaeformis var. perpusilla and A. veneta were found on all five test paints, suggesting resistance to all three biocides. A. exigua was found on paints B, D and E. This species appears to compete successfully when both zinc and tributyltin are present as biocides. These three Amphora species have previously been found to be resistant to copper-containing paints together with Licmophora species (Hendey, 1951). Licmophora was found on all five test paints in this study. Hendey (1951) also found that several Nitzschia species showed slight resistance to copper-containing paints, and particularly resistant was N. closterium. Diatoms of this genus were found in limited numbers on all the paints, but mainly on paint C.

Animal and weed fouling were prevalent on the non-toxic uncoated panels particularly during the summer. B. balanoides and bryozoan colonies were the major animal foulers, increasing in numbers in late summer to replace heavy algal fouling mainly by Ectocarpus and Giffordia which occurred in June and July. Fletcher (1974) also noticed the presence of Balanus species on non-toxic panels in September following the development of the algal climax community. Serpulid worms, bryozoans, sponges and mussels were also found during the summer. Harris (1946) found mussels to be very sensitive to antifouling paints and a good indication of the lack of toxicity of a surface. The diatom species were mainly epiphytic on the fouling algae and few of the species found in high numbers on the SPC test paints were found on the non-toxic panels. No diatoms were found on non-toxic panels exposed in the Yealm estuary by Callow (1986), but Navicula, Stauroneis and Amphora species were found at various sites around the world. Fletcher (1974) found colonial naviculoid diatoms on non-toxic panels at a U.K. site in January, March and June.

The quantitative method of fouling assessment employed in these trials provided a regular profile of fouling on each test paint. High and significant correlation between the fouling variables was attained indicating that they are accurate representations of fouling levels. The test paints in these trials were all of similar formulation and similar fouling organisms with variable fouling levels were expected. Therefore variables such as chlorophyll a concentration, and dry and ashed weights were a suitable measure of fouling. However, when different test paints are to be tested or a wider range of fouling organisms (which may include animal foulers and macroalgae in addition to the slime-film) is anticipated, then an alternative fouling assessment system may be a ranking system for different organisms which relates organism size or weight to coverage of the panel surface (Fry, 1975). The data could then be summed to form a fouling total. Alternatively a means of comparing paints by species diversity could be used as effective antifouling paints reduce the number of fouling species (Robinson et al., 1985).

Both raft trials showed the variation in antifouling performance of the test paints. Data analysis showed that there were no significant differences in the antifouling performances of the cuprous oxide-containing paints A, D and E, even though D and E contained lower levels of cuprous oxide. Zinc oxide was used as a substitute for cuprous oxide in paint B and this paint was shown to have significantly higher fouling levels, at the 95% confidence level, than all the copper-containing paints. Therefore it seems that zinc oxide cannot be used effectively as a complete replacement for cuprous oxide in this paint formulation, but it can be used to partly replace cuprous oxide, as in paints D and E, with no significant loss in antifouling performance compared to paint A, which did not contain zinc oxide. The control paint (C) showed significantly higher fouling levels than all the other test paints. All five test paints were composed of a copolymer matrix and contained tributyltin as the principal biocide. Therefore the addition of either cuprous oxide or zinc oxide (as in paints A, B, D or E) considerably improved the antifouling performance compared to that when tributyltin was the only biocide (paint C). Such high levels of zinc oxide as used in paints B, D and E are not in current commercial use. Antifouling activity was similar when a combination of cuprous and zinc oxide was used (paints D and E) as in the presence of cuprous oxide alone (paint A). Therefore it appears that zinc oxide does not improve the antifouling performance of the paint system but it does allow cost reduction without significant loss of antifouling activity. The cost of cuprous oxide in December 1984 was £1553 per tonne, while that of zinc oxide was £805 per tonne. Therefore complete or partial replacement of cuprous oxide by zinc oxide in a SPC paint would be financially desirable. Izral'yants et al. (1982) also found that a vinyl-matrix paint containing cuprous and zinc oxides at 26.6 and 13.4 percentage volumes respectively showed good antifouling activity. In an epoxy-base enamel containing tributyltin oxide, Frost et al. (1975) found that 25% of the cuprous oxide could be replaced with zinc oxide with no resulting change in the enamel properties and this enamel resisted fouling in the Barents sea for three years. The similar antifouling performances shown by paints

A, D and E, even though the last two paints contained proportionally less cuprous oxide, may be the result of a synergistic toxic action between copper and zinc as found in laboratory growth experiments on axenic cultures of Amphora and Amphiprora (French, 1985). In addition, or alternatively, since the presence of zinc oxide in paints D and E has been found from leaching tests to result in increased copper leaching rates from the test paints (French, 1985 and French et al., 1985), it may be due to this.

Raft trials 1 and 2 also compared the relative influences of increasing exposure period (trial 1) and of seasonal variation (trial 2) on the fouling levels on the five test paints. The dominant effect of season was apparent. The main fouling peaks were January to May and August to November. At these times fouling differences between the test paints were most clear and the greatest diversity of diatom species was found. The results suggest that a better test of the antifouling properties of paints could be made under conditions of peak fouling. Raft exposure times could perhaps be reduced by immersion over periods of peak fouling which may facilitate the use of more than one test site to allow paint testing under different fouling conditions at sites with different indigenous populations. Peak fouling periods at the different test locations would need to be established and physical features of the paints which may vary with length of exposure could be determined by other means, such as immersion on a rotor apparatus for biocide leaching tests (French, 1985).

A high proportion of the fouling organisms on the SPC test paints were diatoms and they must compete under the influence of seasonal changes as well as in response to the presence of antifouling biocides. Irradiance levels vary with season and will influence the growth of fouling organisms. Growth levels may also follow the seasonal temperature variation. Low temperatures and low irradiance levels could account for the higher levels of fouling found on the SPC test paints during the months November to January. Reduction in fouling in summer may partly be a result of grazing by zooplankton. Salinity and pH also vary with season and the fouling peaks corresponded to pH values lying in the range 7.8-8.0 and salinity values in the range 32.5-34.5% (French, 1985). Seasonal changes in river outflow may also influence seasonal production (Kirk, 1983) and this may have some effect on fouling levels on panels exposed in the Yealm estuary.

Five replicate test panels of each SPC test paint were sufficient to distinguish the cuprous oxide-containing paints, A, D and E from paints B and C. They also diffferentiated between paint B containing tributyltin and zinc oxide as biocides and paint C with only tributyltin. However, had a greater number of replicates been used, significant differences in fouling levels on the copper-containing paints may have been found, but when a study was made of the occasional times when significant differences between these three paints was found, no consistent order of fouling levels was apparent. Therefore, it is unlikely that these paints could be shown to differ significantly and consistently in antifouling performance with higher replication.

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