

POLYMERS IN A MARINE ENVIRONMENT

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BY

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This International Conference, sponsored by the Institute of Physics, The Royal Society of Chemistry, and the Institute of Marine Engineers, was held on 31 October to 2 November 1984 with the aim of bringing together practical and fundamental work relevant to applications of polymers in ships, ports, harbours, and offshore. Two papers were presented by staff from ARE (M3) Holton Heath, one dealing with the mechanism by which water can affect the properties of a rubber compound, the other with experiences of the anti-fouling capabilities of various rubber compositions. The Conference was divided into six sessions, one session being for poster papers. Staff from ARE (M3) attended the last four sessions (1 and 2 November) and this note aims to highlight subjects from these sessions which are of relevance to current and future materials requirements of the Royal Navy.

Session III was concerned with the interaction of water with polymeric materials. One of the poster papers (Paper IV 6) was very relevant to Session III: it dealt with the inherent resistance to seawater of natural rubber tyres which showed no measurable reduction in strength or modulus after being recovered from a supply ship sunk in 1941. However, in Paper III 2, which was concerned with water uptake by hydrocarbon rubbers, it was shown that the presence of small quantities of water-soluble impurities greatly increased water uptake. Paper III 2 dealt in detail with the diffusion of water in polymers and the effects of hydrophilic additives in the polymers. These papers and that presented by M. R. Bowditch of ARE (M3), Paper III 6, came to very similar conclusions on the water uptake of rubbers: first, that water dissolved in the polymer matrix acts as a plasticizer and lowers the glass transition temperature; secondly, compounded rubbers can absorb far greater amounts of water than can be accounted for by the solubility of water in the basic polymer matrix; thirdly, that much of the water occurs as droplets associated with filler particles containing very small amounts of soluble species; and fourthly that osmotic effects are significant in determining the amount of water present, at equilibrium, in a compounded rubber. One positive message was that degradation of polymeric material properties caused by water uptake can be reduced or avoided if compounding ingredients are selected on the basis of their content of water soluble material. For example, polysulphide rubbers cured with soluble chromates are badly swollen by water but use of less soluble curing agents can give more durable, water-resistant sealants; and polyurethanes reinforced with barytes show a significant reduction in modulus due to water uptake whereas the use of iron oxide fillers yields material which is only slightly affected.

Degradation of the properties of other polymeric materials by water can also be dramatic. Paper III 3 dealt with stress crazing of polymethylmethacrylate (Perspex) by water, and Paper III 4 with the breakdown of polyurethane foam insulation, used in the transportation of liquid petroleum gas.

In Session V, three papers dealt with the problem of assessing the dangers of smoke and toxic gas arising from polymers in a shipboard fire situation, and the fire resistance of polymeric materials. The great variation in the temperatures experienced during a fire leads to corresponding variations in the nature of the decomposition or combustion products of polymeric materials. Even accepting these limitations and uncertainties, two areas were highlighted where materials with better fire resistance and reduced risk of toxic smoke formation were needed: cable insulants and foamed polymers.

In Session VI three papers dealt with diverse aspects of paints and painting; the other five papers in the session covered aspects of marine fouling and its prevention. In this well balanced sequence of papers on fouling the basic mechanisms, as far as they are established, by which fouling develops were expertly described (Paper VI 4), followed by two papers on the use of toxins to prevent fouling, and finally two papers which described antifouling treatments which were environmentally far more acceptable in that they depended on the surface properties of the coatings used rather than on poisons. The value of tributyl tin compounds as toxins, and their incorporation in self-polishing copolymer (SPC) paints were described in Paper VI 5. Poster paper IV 3 also dealt with SPC paints, and demonstrated, through raft trials, that cuprous oxide was a necessary toxin in addition to the tributyl tin methacrylate copolymer. Some of the detailed analytical work on SPC paints after immersion in seawater was very revealing, and indicated that a thin ($\sim 10 \mu\text{m}$) gelatinous layer formed on the surface of the paint, probably a necessary step in the self polishing process. The ARE Paper VI 6 described the performance of various rubber formulations in raft trials. Only rubbers containing tributyl tin compounds were consistently effective, but even these materials allowed some primary slime formation, casting doubt on their long term (>10 years) performance as anti-fouling coatings. The final paper of the session, Paper VI 8, described the successful use of a fluoropolyurethane paint which incorporated nearly 40% of polytetrafluorethylene (Teflon) to give a durable 'non-stick' surface. Some fouling does occur but it can be removed with fairly mild scrubbing, and the technique should be of use in some areas of application. The paper presented by International Paint (Paper VI 7) described an exciting alternative to the market leaders (the SPC paints), and Shell displayed a similar development in the exhibition. These products are silicone rubbers containing a few percent of silicone oil, and they appear to be true anti-fouling coating materials. Shell claim that they operate through the silicone oil being exuded from the rubber, but International Paint presented an elegant explanation which did not require any loss of the oil from the rubber. Instead, it was suggested that the surface presented by the oil-impregnated rubber immersed in seawater physically repels fouling organisms. Panels were shown which had resisted fouling even after ten years in the sea.

The overall impression was of a well-organized conference which encouraged informal exchanges of views during the lunch and coffee intervals, as well as more formal discussions at the end of each session. The two areas of particular interest to ARE (M3) were, naturally, associated with the subjects of the papers they presented, and the encouragement derived from the Conference should stimulate further work in water uptake of polymers and anti-fouling rubber formulations.