Abstract

Fluoropolymers possess a number of unusual properties which should prompt wide usage in marine applications: (1) exceptional resistance to the effects of water, sunlight and biological organisms, (2) non-wetting, fast-draining surfaces, (3) low friction or dry-film lubricant properties, and (5) special properties such as high thermal stability of poly(tetrafluoroethylene) and easy moldability of fluoroepoxy. Fluoropolymers are not widely used in marine applications and the initial cost is most often cited as the reason.

1. Introduction

The environment of the ocean surface is extremely damaging to organic materials and to most metals. The combined effects of salt water, fresh water (rain and condensate), harsh sunlight, temperature variations, a plethora of hungry living creatures and physical abuse are enough to disjoin or dislodge most of man's constructions rapidly. Because of this, it is prudent to consider the most naturally resistant of materials for use on the sea aboard structures which are worth saving for substantial periods of time. In the realm of organic substances, the fluoropolymers are probably the ultimate materials by most criteria, and yet, they are not widely used in marine applications. It is an oversight which should be corrected.

2. Water Effects

No organic material is totally impervious to the diffusion of molecular water; however, there is a wide range of reaction to water exposure by polymeric materials. Those containing molecules composed of much oxygen or nitrogen, such as polyethylene oxide or polyacrylamide, will dissolve. Those such as nylon or epoxy absorb several percent of their dry weight of water. Polymers based upon hydrocarbon alone, such as polystyrene or polyethylene, absorb small amounts, and those composed of only fluorocarbon such as polytetrafluoroethylene (PTFE) come as close to total non-absorption as is possible with organic materials.

There are some generally known preconceptions regarding PTFE in particular which tend to compromise thought regarding it as a superior water barrier. In particular, it is known that the most common method of use as a coating, which entails spray application as a suspension and subsequent high temperature fusion, produces a coating which is somewhat porous. Even though the PTFE itself is extremely hydrophobic, there are holes in the coating which allow moisture entry to a surface beneath. In an uncommon method of use, the suspension of PTFE particles in a fluorinated epoxy or fluorinated polyurethane matrix, there is no opportunity for the same type of physical holes to develop, and only the extent of hydrophobic compromise introduced by the reactive groups influences absorption. Thus, it is possible to make easily-used materials which are very hydrophobic and useful as marine coatings [1,2].

3. Sunlight Effects

Theoretical treatments of the effects of electromagnetic radiation upon polymer properties are often marginally useful at best for the assessment of relatively resistant materials in harsh environments because of the multiplicity of factors involved, such radiation wave lengths, absorption frequencies, energy transfer efficiencies, impurity effects, bond energies, etc. Practical arguments based upon actual performance are often much more relevant to the real situation, and on such a basis, the case for fluoropolymers at sea is a strong one. On clear days, not only the direct radiation from the sun, but extensive...
specular reflection from wavelets of the water surface subject a seaborne, external area to a greater radiation dose than would normally be received on land. This is a significant factor in the loss of gloss, checking, cracking, peeling, hardening, color fading, and generally rapid deterioration of topside marine paints. If it is considered that the coatings applied to siding materials for houses are expected to last for at least 20 years, and that the fluoropolymer coatings are regarded as "top-of-the-line" in this field, a reasonable case is made that such materials should be used where they are so obviously applicable -- at sea.

There are some practical difficulties involved in the direct utilization of house siding technology on vessels, but it is possible today to bring a similar technology to bear upon the marine case. New materials such as fluoroepoxies, fluoropolyurethanes and fluoroacrylics can overcome the application difficulties [3,4]. Although specific development to prove cost-effectiveness is yet to be demonstrated for these materials, the opportunity for greatly increased light stability is such that the development effort is worthwhile.

4. Biological Organisms

The ocean is marvelously rich in living creatures, all of whom ingest something for sustenance. Fluorocarbon is not part of the natural diet of any, and the eating of a fluoropolymer by a marine organism would at best be non-nutritious and at worst, fatal. Certain organisms, such as barnacles, may incidentally damage a fluoropolymer surface, but the heavily-fluorinated polymers would be sought by none as a food source. Also, certain polymers, such as PTFE, do not provide a certain footing for adhesive-type organisms. Living organisms also generate waste products as a result of metabolism which can have severe effects upon organic materials. The chemical inertness of the pure fluoropolymers (that is, those that contain no elements in addition to carbon and fluorine) is such that resistance to marine waste products should be superb.

5. Anti-Adhesive Surfaces

In a previous paper [2], the concept of a "fouling release" coating, as opposed to an "antifouling" coating, has been developed. Basically, the idea is that no man-made adhesives can adhere to virgin PTFE, and if the material can be applied practically to underwater portions of ship hulls, marine organisms should be at least easy to remove from the surfaces. It is suggested as an alternative approach to the marine fouling problem vis-a-vis toxic anti-fouling paints. The fouling release concept needs extensive development and proof, but as a result of several years of limited testing, there is little present doubt that the approach is technically feasible. Economic and logistic problems need to be minimized in order to realize the special anti-adhesive properties of fluoropolymers in marine applications.

6. Low and High Friction Coatings

A film of PTFE has a low coefficient of friction, and a fluorinated epoxy film containing suspended PTFE has a similar low coefficient. However, if PTFE is not included in the fluoroepoxy film, such a film has a relatively high coefficient [5]. This ability to obtain either a low or high friction in a material which is conveniently used could be most useful in a variety of marine applications. For example, any place where there is metal-to-metal contact needing lubricity, the PTFE-containing fluoroepoxy would be a candidate for durable lubrication. On the other hand, places which require good footing such as stairs and ladders could profit from the high frictional properties of the fluoroepoxy containing no PTFE. With further development, these materials should also make superior deck coatings--water-resistant, light-resistant and of a high frictional nature.

7. High-Temperature Coatings

There are many places aboard a vessel which become relatively hot, but not extremely hot, at which PTFE coatings would perform well. It has not been used extensively on such locations because of the high-temperature fusion requirement. However, a technique of flame-fusion has been devised which, if employed, would allow many hot areas to be PTFE coated [6]. Because of the high failure rates and frequent repainting needed at such locations, the use of PTFE should be highly cost-effective.

8. Other Applications

By virtue of the non-wetting characteristics, clean fluoropolymer surfaces are fast draining, and this property can be of substantial benefit to visibility in rain storms in which
droplets on a windshield run off as streams instead of shimmering as on a normal surface such as glass [7]. Also, it is possible to build an excellent non-adhesive surface for ice from fluoropolymers with silicone additives [8]. Structural uses for fluoropolymers include such possibilities as filament-winding with fluorooepoxy matrix resins, the casting of permanently lubricated bearings from the same type of resins, and the casting of optically-clear transparencies from fluoroacrylics.

9. Conclusion

Fluoropolymers are relatively expensive organic materials, but the ocean is an expensive environment in which to operate. Such operations as dry docking, repairing underway and replacement due to failure can be very expensive. Because of the unique properties that they offer, the established fluoropolymers such as PTFE and newer materials such as fluorooepoxies, fluoroacrylics and fluorinated polyurethanes deserve an opportunity to display long-term cost effectiveness at sea.

References

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