Hybrid Nanostructure of the Anodic Oxide for Polymer Bonding: A Case Study

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Mercury Marine, Inc., the world leader in engineering, building, and providing marine power, is always looking for a means to increase the corrosion protection of the finish on their marine engines. In addition, they seek to eliminate the use of hexavalent chromium from their finishing processes for their products. The engine housings, aluminum die castings, have been conversion coated, electrodeposition primed (EDP) and then finish lacquered. As an alternative finishing process, hard anodizing (Type III) was considered and tested by Mercury Marine. Two fundamental negative attributes of the Type III finish were encountered: 1) the hard anodic finish did a poor job of protecting sharp edges of the machined surfaces of the die castings; and 2) the hard anodic finish did not EDP very well or consistently.

Walgren Company, a manufacturer of turnkey finishing systems worldwide, was involved through the course of investigation for alternative processes. Walgren is working with Mercury Marine to set up a finishing system, from cleaning through e-coating. In the course of designing the new line, which would have included large chillers and a high power rectifier, Walgren suggested the use of an emerging technology for anodizing aluminum, CompCote®, which would dramatically reduce the need for the chillers and would use lower power rectifiers. This would have two effects; 1) it would lower the power consumption hence reducing the operating costs and 2) it would reduce the initial cost of the equipment.

CompCote® is different from conventional anodizing because of microstructural changes to the anodic oxide induced through a modification to the electrolyte. These changes appear to hybridize the ordered nanostructure of the anodic oxide and make the finish more corrosion and wear resistant. In addition, the hybrid nanostructure of the anodic oxide contains islands of conductive polymer integrated throughout the finish; it can sustain a static charge and therefore has better throwing power with EDP, and provides actual sites for chemical bonding with subsequent polymer finishes.

Samples were run at IHC Corporation in Detroit. A significant technical leap noticed was that during subsequent coating, the samples anodized with the composite finish consistently exhibited complete coverage with EDP at 20µ thicknesses. Samples are currently in corrosion testing at the Gulf of Mexico, and show no evidence of corrosion after 6 months in tide exposure testing.

This presentation shows how a consortium can work together to solve an industrial problem. Through scientific anodizing process innovation and finish engineering know-how, the use of this hybrid nanostructure is being investigated to solve a design challenge and fulfill a performance requirement at Mercury Marine, Inc.

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Introduction/Project History

When a major change is introduced to a manufacturing process, all aspects must be considered. The current process, parameters and materials, the reason for change and all aspects of the proposed change must be kept in mind to optimize results and success. The success of the modified process does not only hinge on the improvements of the finished part; it hinges on the ease of modification and the associated costs.

No project manager is typically expert enough to do this job alone. To optimize project results, a team of experts must be assembled to address the various facets of the manufacturing process changes such that success will be manifested in all aspects of the change: from enhanced product performance to dollars saved. The team can be comprised of internal experts; the project leader and colleagues within the company who are familiar with the materials, processes and testing that go into manufacturing a final product. The team can be comprised of outside experts, consultants and service professionals who are tasked by the project leader to furnish the information, equipment and any other service necessary to manufacture the final product; or, what is sometimes best, the team can be comprised of both internal and outside members who work together to solve the problem and bring about successful change.

This case study shows the value of a consortium of industrial partners working together to solve a problem.

In this case study, the proposed change is for the finishing process for marine engine components manufactured by Mercury Marine, Inc., in Fond du Lac, Wisconsin. Mercury Marine, the world leader in engineering, building, and providing marine power, is always looking for a means to increase the corrosion protection of the finish on their marine engines. In addition, they seek to eliminate the use of hexavalent chromium from their finishing processes for their products. The engine housings, aluminum die castings from alloys XK360 and A356, have been conversion coated, electrodeposition primed (EDP) and then finish lacquered. Mercury's targeted goal is to increase the corrosion resistance of the components from 5 years to 8 years. Another goal is to eliminate Cr^{6+} from the finishing process of the engines.

Clearly, significant changes to the finishing process were necessary to achieve the goals. Internal research and testing of alternative conversion coatings showed that non-Cr^{6+} conversion coatings as well as trivalent conversion coatings (Cr^{3+}) did not perform as well as Cr^{6+} conversion coatings. To achieve the primary goal of extended corrosion resistance, new conversion coating formulations did not appear to be sufficient. See figure no. 1. [1]

Because the base metal for the engine components is cast aluminum alloy, the next finish consideration became anodizing. Both conventional technical anodizing (Type II) and hard anodizing (Type III) were tested in conjunction with EDP and finish lacquer. Internal testing determined that the Type III finish gave the desired corrosion performance with heavy total finish thickness. The major concern regarding the thickness of the final finish was in field performance. Not only was the engine system comprised of many complex components, with through holes and recesses that are difficult to coat to the necessary thickness, but the parts experience rapid, sometimes turbulent water flow, both fresh and salt water; and at intake may encounter sand, dirt, shells and other abrasive media. In other words, thicker finishes tend to spall and chip easier than thinner finishes. See figure nos. 2 and 3. [1, 2]

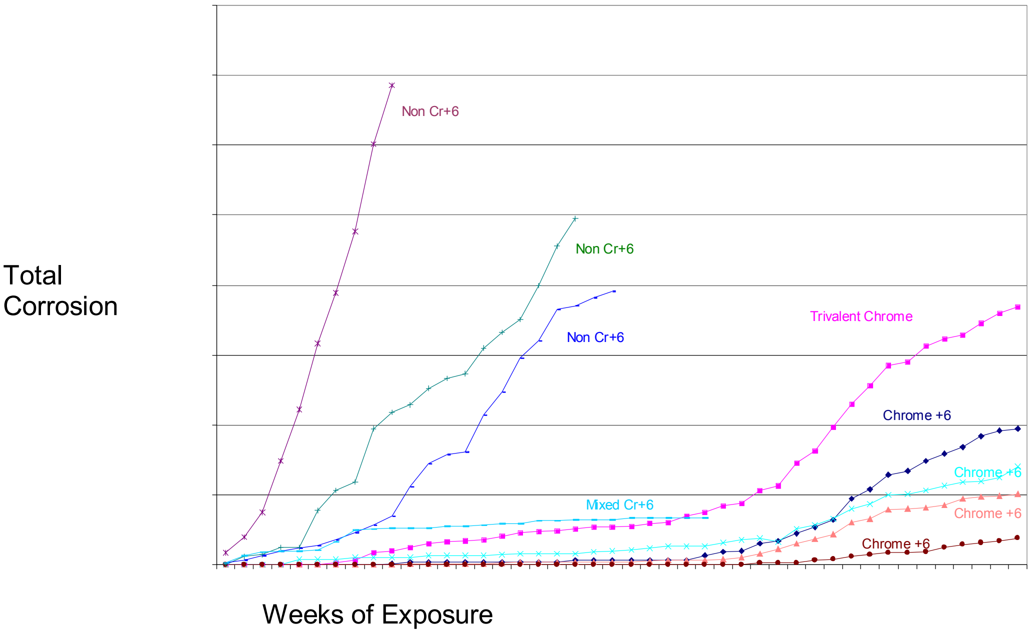

Figure 1: Corrosion testing of various conversion coatings showed consistently that the best performance was with hexavalent chromium containing conversion coatings.

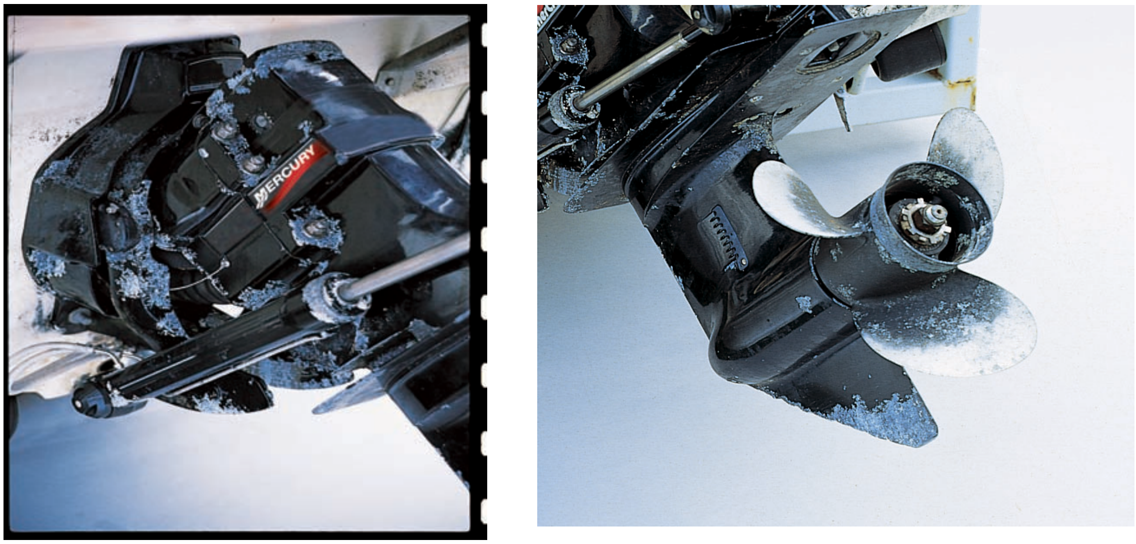

Figure 2: In-field corrosion of outboard engines on the mid- and lower sections of each motor. Note the corrosion initiates and spreads in localized spots. The base and propeller show signs of abrasive wear.

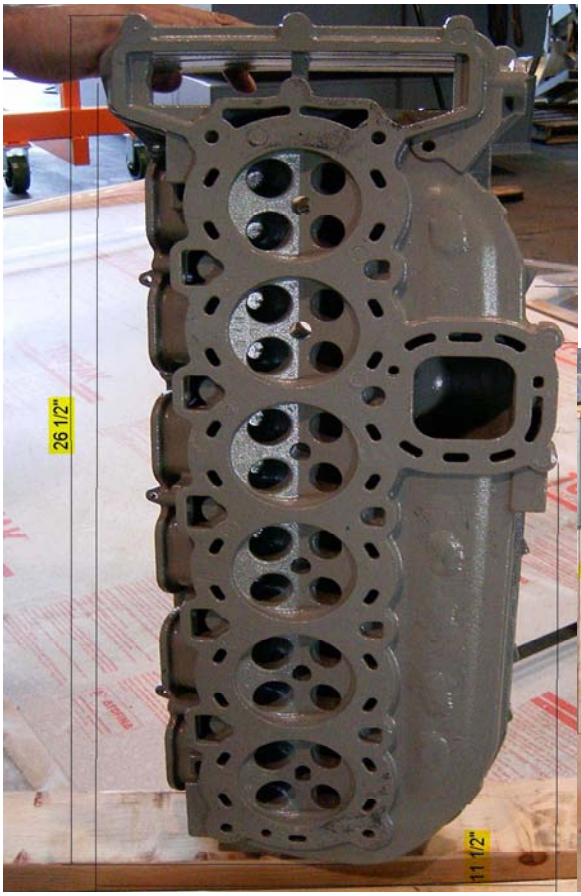

Figure 3: 16 Cylinder head (left). Note the extreme complexity of the part with many small channels and through holes. Not only would the part be anodized, it would also have to be electrodeposition primed. Finish lacquered drive shaft housing (below). The engine components are not only large, they are also heavy.

Two majors drawbacks were encountered with the Type III anodic oxide finish: 1) the hard anodic finish did a poor job of protecting sharp edges of the machined surfaces of the die castings; and 2) the hard anodic finish did not EDP well or consistently. This was due in part to the complex configuration of the castings as well as the inability for the Type III finish to hold a static electrical charge during the EDP process.

Process Development

Walgren Company, in Grand Rapids, Michigan, a manufacturer of turnkey finishing systems worldwide, was contacted by Mercury Marine to provide a finishing system, from cleaning through EDP. The initial customer request included rectification and chilling for a hard coat anodizing operation as the base for paint. Another important part of the request was a budgetary proposal with emphasis on reduced operating cost.

Driven by the request for a more cost effective process with equal or better operating costs, and recognizing the possibility that hard anodizing may be design overkill when considering the multiplicity of layers, the quotation for a line complete with hard anodizing was provided. However, also included was a recommendation to evaluate an emerging anodizing technology called CompCote®, which would dramatically reduce the need for the chillers and would use lower power rectifiers. This would save on the initial equipment cost and the total operating costs.

CompCote®, hereafter referred to as the composite finish, is an anodizing process which incorporates electroactive polymer into the sulfuric acid electrolyte, resulting in modification of the nanoscale structure during anodizing and includes the electroactive polymer within the hydrated aluminum oxide of the anodized finish. The polymer is chemically bound to the anodic oxide and experiments have shown it cannot be extracted with solvents specific for that type polymer.

Similarly driven by the desire for a more cost effective process with equal or better operating costs, and the reports that the composite finish would perform equal to or better than hard anodizing for this application, Mercury provided samples to IHC Corporation in Detroit, Michigan, for finishing with the composite finish to evaluate the basic performance through EDP and finish lacquering. The finish sequence was specified identically to that for hard anodizing, and the die cast samples were anodized with twenty microns (20µ) of the composite finish and resubmitted to Mercury Marine for EDP.

The "leap" of the composite finish technology was that in subsequent electrodeposition prime processing, it exhibited consistent and total coverage, even in the recesses and through holes of the most complex castings. EDP could therefore be used, in conjunction with the composite finish, for additional corrosion protection in areas that were typically difficult to coat. The next consideration for the composite finish was evident for the project: the possibility for the use of a thin layer of the composite finish (up to 5µ) as a direct replacement for traditional Cr^{6+} conversion coatings. These samples are currently being prepared for testing.

Engine components finished with 20µ of the composite finish, EDP'd and finish lacquered are currently in corrosion testing at Mercury's facility at the Gulf of Mexico in Florida. They have been in testing for over 6 months and show no evidence of corrosion. See figure no. 4.

Figure No. 4: Documentary photograph of gear cases with several different types of coating systems being tested in the tidal range of the ocean. Test duration is typically 1 year. The composite samples have been in test for over 6 months.

Characterization of the Composite Finish

In order to understand the ability of the composite finish to be reliably electrodeposition primed, testing and analysis performed in the past with the finish used as a transition layer for polymer-metal bonding were reviewed and summarized [3 – 5]. Based upon the results of these studies, the conclusion for the current new application is that the composite finish, although not conductive, has the ability to sustain a static charge. The ability is derived from the presence of islands of conductive polymer integrated throughout the anodized finish. Because it can hold a static charge, the composite finish workpiece exhibits better throwing power through the EDP process. The islands of conductive polymer also function as bonding sites for subsequent polymer layers, enhancing adhesion and therefore corrosion resistance of the finish system.

Analysis Summary

Comparative engineering testing by way of light fastness, adhesion and dye permanency testing was performed on samples finished with standard Type I, II, and III anodized finishes and samples finished with the new composite anodic finish for aluminum. Testing determined differences in performance between the samples anodized following conventional practices with standard electrolytes and samples anodized with the composite finish. Comparative scientific characterization of the finishes was also performed utilizing Transmission Electron Microscopy (TEM), Scanning Electron Microscopy with Energy Dispersive X-ray Spectrographic Analysis (SEM/EDS), high power Fourier Transform Infrared Spectrographic (FT-IR) Analysis, and X-ray Photoelectron Spectrographic (XPS) Analysis.

Comparative analysis within the TEM determined the nanoscale structure of the composite anodic oxide finish appeared hybridized between the unidirectional columnar finishes of the Type II and Type III finish and the skewed-appearing Type I finish. The fact that the composite finish process, following traditional process parameters for Type II and Type III finishes, yielded finishes of equivalent thicknesses, indicates that the addition of the conductive polymer to the electrolyte does not inhibit finish growth as with the chromate ion in a Type I process. See figures 5 and 6.

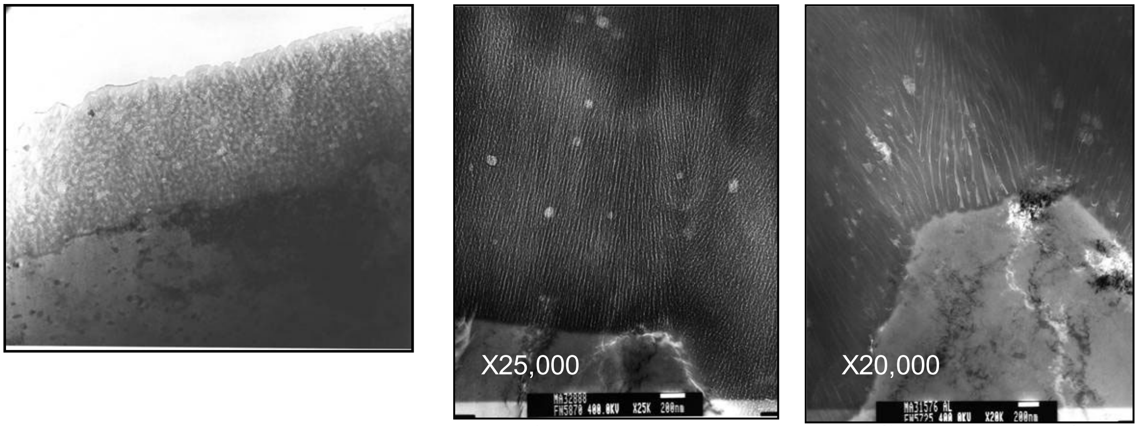

Figure 5: Documentary photomicrographs of the nanoscale structures of (from left to right) Types I, II and III anodic oxide finishes. Note the absence of unidirectional columns in the Type I finish.

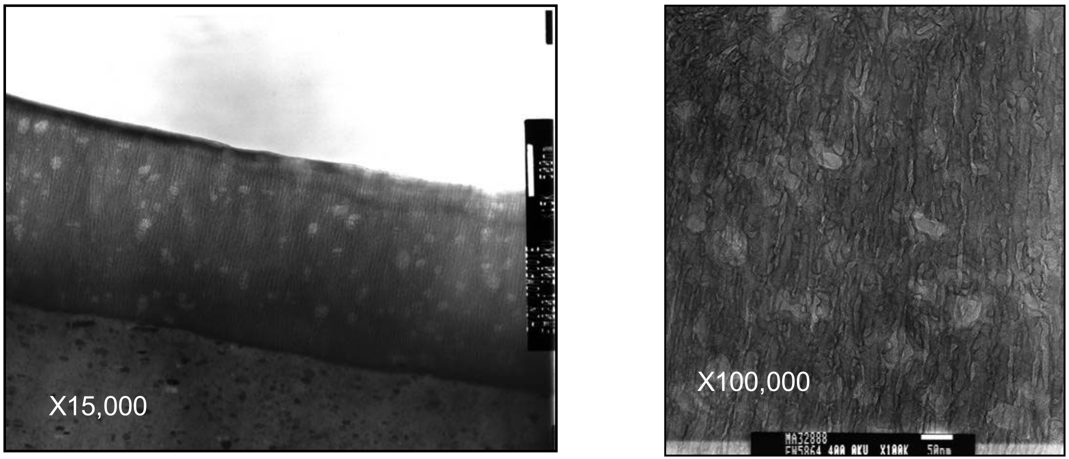

Figure 6: Documentary photomicrographs of the hybrid nanoscale structure of the composite finish. Note while the columnar character of the structure is maintained, it appears disrupted.

Samples of the composite finish were screen printed with ink typical for outdoor measurement equipment and compared to samples finished with Type II anodic oxide and screen printed with the same ink. The ink-finish interface exhibited evidence of interaction between the ink layer and the finish microstructure within the first 40 nm of the composite finish. EDS across the interface revealed the presence of chlorine, a constituent of the ink, not characteristic for the composite anodizing process. The ink-Type II finish interface was clearly delineated with evidence of delamination; no intrusion of the ink within the porous structure was noted. These results strongly indicate the ink and the composite film indeed reacted together, producing a well-bonded interface. See figure no. 7.

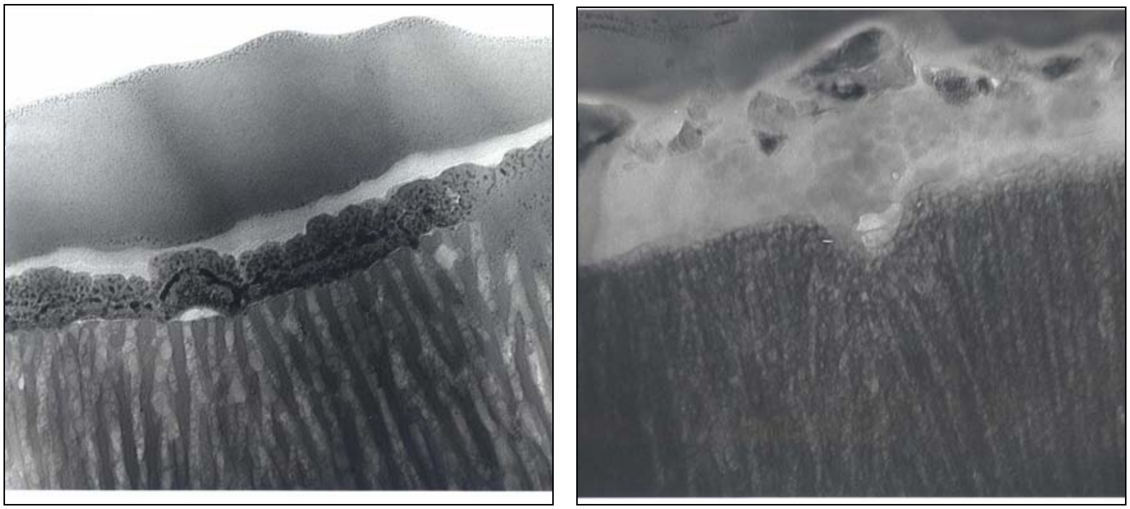

Figure No. 7: Comparative screen printing of conventionally anodized, Type II finish (left) shows no intrusion of the ink into the columnar structure. The composite finish (right) shows ink intrusion 40 nm into the anodic oxide structure.

TEM sections of a Type II unsealed anodic film and composite films were analyzed by way of high intensity Fourier Transform Infrared Spectrographic analysis. The energy source for the instrument was hooked up to a synchrotron light source at Brookhaven National Laboratory in Brookhaven, New York. The resolution of the instrument was 4 –5μ.

The trends in the infrared data collected from the bottom of the conventionally anodized finish to the top strongly suggest a shift in the formation and amount of active hydroxide and sulfate groups. The Al-O feature at approximately 750 cm^{-1} dominates, but shifts upward in the spectra as the sulfate peaks at 1000 to 1100 cm^{-1} become larger and more defined. With the development of the sulfate absorption, hydroxide absorption becomes pronounced. This actually makes sense, as the surface of the anodic film, regardless of type or formulation, should exhibit more hydration.

The composite finish exhibited evidence of inclusion of the electroactive modifier with absorption in the higher IR. The spectral shifts toward the higher IR were noted from the substrate, where the inorganic absorbances were most pronounced to the middle and finally the surface portions where absorption of both OH^{-1} and carbon-based inorganic salts were detected within the composite polymer-oxide finish. See figure no. 8.

The XPS results show conclusively the inclusion of fragments of the electroactive polymer modifier. Saturated and π- conjugated carbons were noted. Probably the most significant ligands determined regarding the possibility of functionality and therefore bonding to subsequent polymers, were carbonyl linkages, bound to the disordered (hydr) oxide structure. The C=O and –COOH groups are powerful electron-withdrawing groups, and therefore would be expected to react with subsequent polymer additions through electrophilic addition, forming stable intermediate compounds between the composite finish and the paint, adhesive, or any other polymer layer [7].

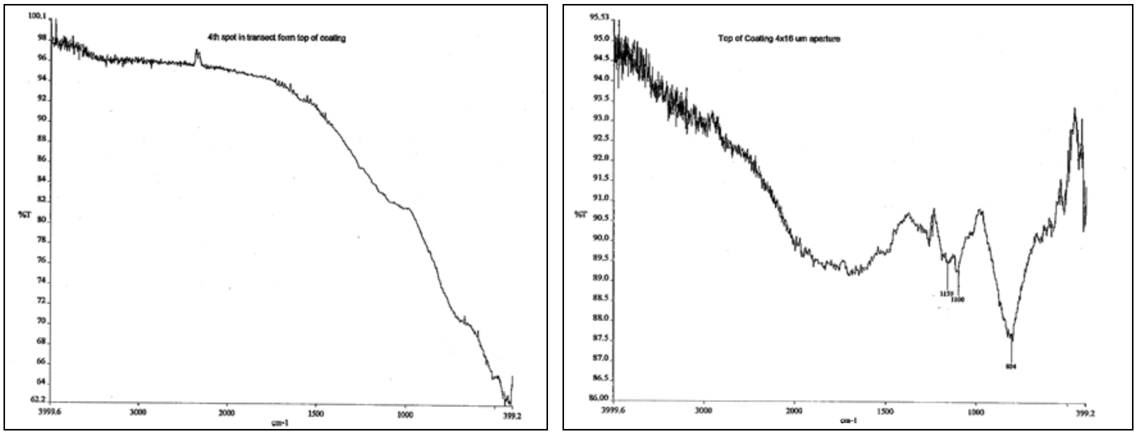

Figure No. 8: High power FT-IR show distinct differences in the composition of the conventionally anodized Type II finish (left) and the composite finish (right). IR absorption in the higher wavelengths is typically for organic materials and the absorbances are typical for the electroactive polymer additive, proving its presence within the anodized finish. .

TEM analysis of a sample that had been finished with the hard version of the composite finish, hot water sealed, treated with a bonding agent and over molded with rubber, then vulcanized, disclosed the presence of fibrils bridging the interface between the finish and the subsequent polymers. Images of a sample that had been anodized, dichromate sealed and similarly treated with the bonding agent and over-molded did not exhibit these fibrous “bridges” [6]. Upon consideration of the sample orientation during high intensity FT-IR analysis, 4-5µ on a short transverse section at the surface, and the depth of analysis during XPS, 0 – 30 Angstroms from the surface, the fibrils imaged at the composite finish – bonding agent interface during TEM analysis may be an intermediate compound formed between the organic linkages identified as present within the composite finish and the bonding agent/adhesive. See figure no. 9.

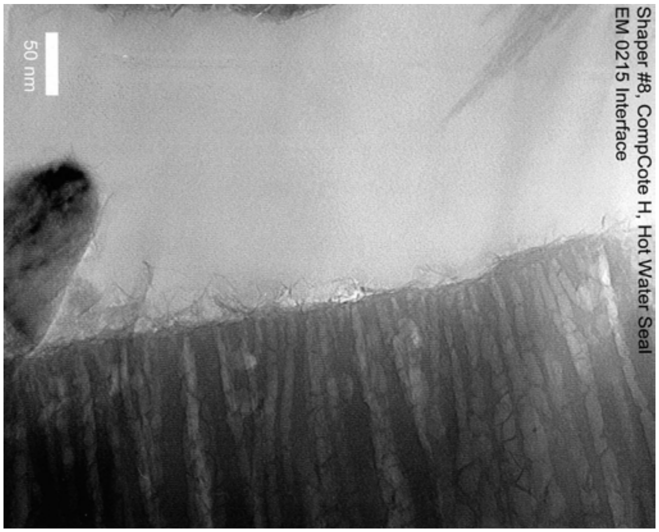

Figure No. 9: TEM image of the interface between the surface of a composite finish processed by way of Type III anodizing parameters and treated with a bonding agent then over-molded with rubber and vulcanized exhibited fibrils extending from the surface of the finish into the polymer layer. EELS analysis of the fibrils determined they were indeed carbon based. No other anodic oxides treated in the same way exhibited these fibrils.

Improved light fastness of the composite finish by a factor of three over samples with a standard Type II anodic finish was determined. These results are believed to be the result of the modification of the anodic finish nanoscale structure introduced through the addition of the electroactive polymer to the anodizing electrolyte. The more cellular structure would result in scattering of light within the finish, rather than direct reflection as would be the case with the unidirectional columns of the typical Type II nanoscale structure. Direct reflection would tend to degrade the dye molecules through photo initiated oxidation [8]. Another possibility to consider would be that the retained polymeric ligands might bind with the dye, improving the stability of the color within the finish.

Conclusion

The results of the engineering tests and the scientific characterization strongly suggest the composite coating, because of the retention of the organic ligands, is a binding surface for subsequent polymer layers. Furthermore, by virtue of the polar nature of a polymer ligand, the surface will be able to hold a static charge, enabling the success of the EDP process for the Mercury Marine engine components.

Therefore, the composite finish offers the first true transition layer that enables actual chemical polymer-metal bonding through both direct application and electrodeposition processes. In addition, the composite finish is heavy metal free, making it a viable alternative to conversion coating which may not exhibit complete coverage through immersion processing and contain chromium.

The preceding experimental results also indicate that in specifying finishes for applications normally relegated to Type I, II and III anodic oxide finishes, serious consideration can be given to the composite finish. Should actual application tests determine the composite finish performs comparably to any of the conventional processes, added benefits can be derived in the form of energy savings, as the oxide formation current density is lower for Types I and III (it is equivalent to the Type II process) and the process temperature is ambient for the composite finish. In addition, the chrome-free electrolyte avoids pollution hazards and waste treatment costs associated with Type I anodizing processes.

The consortium of Mercury Marine, Inc., Walgren Company, CompCote® International, Inc., and IHC Corp., exploited the properties of an emerging technology and discovered a new capability and applications. However, the success of the application will be determined through the results of the corrosion study currently underway.

JMR, 25 September 2006, JMJ

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