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STUDY OF IMPACT ON FUEL ETHANOL IN CONTACT WITH COATINGS ORGANOMETALLIC AND TINNED USED IN STEEL PLATES FOR FUEL TANKS MANUFACTURING

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Abstract. *The automobilist industrial is considered the most competition sector of economy. Currently, a strategic factor among companies in the industry is the ability to provide fast response to market demands, from the development and introduction of new products. To meet this demand, the coatings that cover the surface of the steel plates were developed in order to protect metal surfaces against corrosive environment. The coating most used for fabrication of fuel tanks are organometallic and tinned, seen that both have good performance against corrosive environment. When the ethanol has contacts with constituent metallic materials of various carrier systems, Can become harmful and may cause the metal oxidation in the fuel tank. Seeing that the ethanol have harmful factor when in contact with coatings, the present work purposes to study the behavior of ethanol, when stay in contact with organometallic and tinned coatings inside the tanks of automotive fuels, taking into account the oxidative behavior of coatings. The impacts in fuel ethanol using organometallic and tinned coatings, has extreme importance, because when consider the results related to the damage caused by contamination in fuel due to the corrosion of coatings and obstruction of internal engine components.*

Keywords: *fuel tanks, tin coating, organometallic coating, rust, Ethanol fuel Introduction.*

The automotive industrial and economic sector, is one of the sectors of the economy in which competition is fierce and faces more challenges. The development and introduction of new products, in order to obtain faster responses to market demands, have been considered strategic factors between the companies in the industry. Suppliers and automakers are thus continually challenged to meet the demand for better quality, lower cost and better efficiency for automotive assembly lines (Gang et al., 2004). This manifested through investments in modernizing existing plants and modifying the product, investment in technology and specialization of labor, the work of planning and development sectors so that the company is prepared for the current market.

The main factor to be taken into account is the cost, as it has greater impact on competitiveness by technological complexity in product development and manufacturing process. Another factor that is becoming increasingly important is the environmental issue, not only for pollution caused by greenhouse gas emissions, but also for recycling, life cycle of components and use of heavy materials in the manufacture of vehicles that has significant impacts on society in social and environmental terms. (Sabila, 2013).

Because the burning Ethanol emit greenhouse gases such as carbon monoxide (CO) and hydrocarbons (HC) generated during incomplete combustion reaction that occurs in the engine, the fuel system is the most polluting source. Therefore, manufacturers choose to develop designs for obtaining lighter vehicles in order to reduce fuel consumption and therefore reducing the polluting gases into the atmosphere. It is known that reducing the weight of vehicles has the advantage of economy of 3 to 7% of fuel for 10% weight reduction, with a consequent reduction of the emission of pollutants (Suzuki, 2007).

The development of a fuel system costs, corrosion resistance and decrease in environmental impacts are strong and crucial concerns, causing automakers seek responsibility for developing their suppliers increase efficiency. The challenge is to innovate and provide quality fuel system that meets all the engineering specifications at a competitive price.

Addition to concerns about the environment, today's automakers are also concerned with the quality of parts from its suppliers with respect to corrosion. This is an important property to be evaluated in the materials, particularly in tanks of fuel, because the use of petroleum-derived fuels and biofuels, in contact with the metal, can lead to metal corrosion. This process is the transformation of a metal material or metal alloy by chemical or electrochemical interaction in a particular means of exposure, resulting in the formation of corrosion products and energy release (Gentil, 2007).
In the mid-60s, with the goal of finding a solution to the corrosion resistance problem, organometallic coating technology is designed, developed in the United States by the company Diamond Shamrock Co. The process consists of a metal-based coating lamellar flakes of zinc and aluminum in aqueous solution in the league chromate, improving the action of aggressive chemicals, and the absence of absorption of hydrogen embrittlement (released in the chemical reactions during deposition). Over the years, new technologies have emerged to improve technology aimed at improving the product, which now includes the concern with performance and environmental impacts. Today the organometallic technology follows the same steps of the above, but the water-based and free of Cr + 6, recognized as carcinogen (Suzuki, 2007).

The impact on fuel associated with the use of tin and organometallic coatings, are extremely important, especially when you consider the results related to damage caused by contamination in fuel due to the corrosion of coatings. (Kuri, 2009).
Attempt to produce cars of higher quality and competitiveness, it was necessary to use organometallic coatings and tinned to minimize corrosion caused by fuel ethanol. What makes the potentially harmful Ethanol to metallic materials, is partly because of this fuel have mostly chlorides and additives, which are usually found in adulterated ethanol. which directly impacts fuel burn and consequently the engine performance.
Then as the fuel ethanol has damaging factor in contact with coating, this paper aims to study the fuel ethanol behavior when in the presence of organometallic and tin coatings within the automotive fuel tanks, taking into account the oxidative behavior coatings.

1. EXPERIMETAL PROCEDURE

To simulate the fuel tank was necessary to conform the sheet steel cups shape and subsequently coat them with organometallic tin coatings and exemplified in Figure 1. These samples were provided by SASFT. The fuel ethanol used was the same as for supply of automotive vehicles and was provided by REGAP - Gabriel Passos Refinery - Petrobras, located in Betim, Minas Gerais.

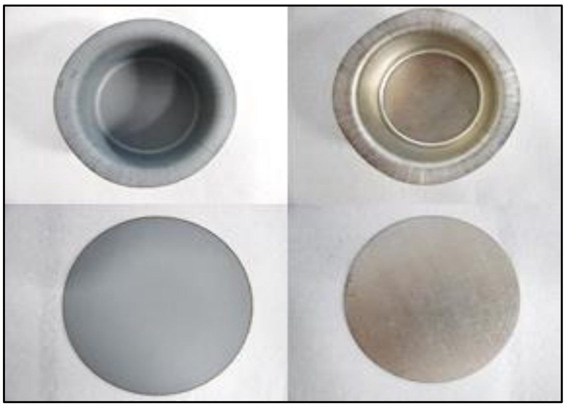


FIGURE 1 - Specimens "cups and lids" coated with Tinned coatings and Organometallic respectively.

Initially, samples were prepared in triplicate, organometallic samples and tinned with their respective caps, Trucks through an analytical balance (MettlerToledo) four decimal places and their masses were noted, soon after the pieces were photographed to visually be compared in end of test. In each beaker was added 30 mL of ethanol fuel, then sealed with the aid of a oring (fluoroelastomer materials) and capped, after these were sealed with screws to prevent leakage of fuel, as demonstrated in Figure 2.

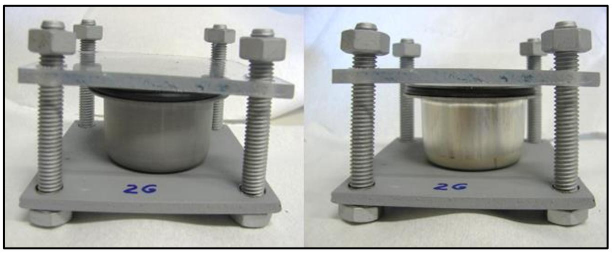


FIGURE 2 - Specimens "cups and lids" coated with Tinned coatings and Organometallic respectively.

To simulate the temperature of the fuel in the vehicle in operation, using an oven (480 EEVF-U / L) was-conditioning the samples at a temperature of 60 ° C +/- 5 in 8 hour cycle time was needed and heated 8 hours with the stove off for a period of 26 weeks. Every 2 days, the test samples were shaken by hand to maintain the homogeneity of the fuel inside the cup, and every four weeks was carried out replacing the ethanol fuel. Every step of the exchange Ethanol, the samples were analyzed visually checking whether there were changes in their coats if evidenced some oxidation principle, the samples were photographed and Ethanol was collected for analysis aspect, color and pH. If there were no change in the characteristics Ethanol was discarded. For pH analysis was performed using the pH meter (METTLER TOLEDO). All the results obtained were recorded and at each change of fuel, the cups and the Ethanol were photographed.

After 26 weeks were terminated cycles analysis, the samples were removed from the oven, cleaned dried in an oven and photographed. Fuel Ethanol was collected and analyzed again, which had changed its characteristics were put in the oven to volatilize and its dry residue collected for further analysis. The cups were weighed and its mass recorded. After this case the samples were suspected to corrosion and the residue dry ethanol were taken for analysis on SEM (Scanning Electron Microscope) and can produce high resolution images of the sample surface and detecting the presence of metals in the residue Ethanol .

CHARACTERIZATION TECHNIQUES

For the analysis of microstructures characterization jacket and ethanol after the tests were used to Scanning Electron Microscopy (SEM) and energy dispersion spectroscopy X-ray (EDS) .- The Scanning Electron Microscope (SEM) is one of the instruments versatile for observation and analysis of the microstructural characteristics of solid materials, providing rapid information on the morphology and identification of chemical elements thereof. The high depth of focus (image for three-dimensional appearance) provides images of up to 300,000 fold increase, allowing more detailed analysis of the compounds and phases formed in the material, compared to the optical microscopy (DEDAVID, 2007). The dispersive spectroscopy X-ray (EDS, or EDX) is a SEM of resources that enables compositional analysis of materials. This electron probe microanalysis technique consists in measuring characteristic X-rays and issued a microscopic region of the sample bombarded by an electron beam. As the lines of characteristic X-rays are specific to each of the sample structure and each element has a unique atomic structure, its wavelength or its power can be used to identify the element that is emitting radiation (Goldstein, 1981).

2. RESULTS AND DISCUSSION

After past 26 weeks, the bodies of evidence went through several tests to better evaluate the coatings studied.

PPEARENCE AND COLOR

Initially, the bodies of evidence and organometallic tin coating were evaluated visually for possible corrosion points. As demonstrated in Figure 3, the coating presented a color difference, the peeling surface, i.e., oxidation was evident test piece tin coating, thereafter all other analyzes were performed from this specimen (coated tinned).

a) b)

Figure 3 - Specimens after durability test. (a): Cups with tin coating; (b): Cups with organometallic coating.

Next, in Figure 4, are presented the images of ethanol which was contained in the specimen from the tin coating before and after the 26 weeks of the test, where it underwent several analyzes to verify the possible contamination due to corrosion displayed on the test piece tin coating.

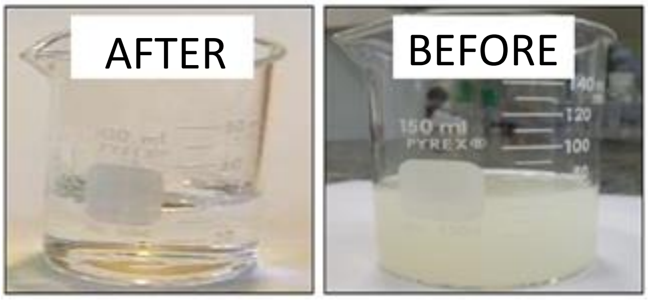
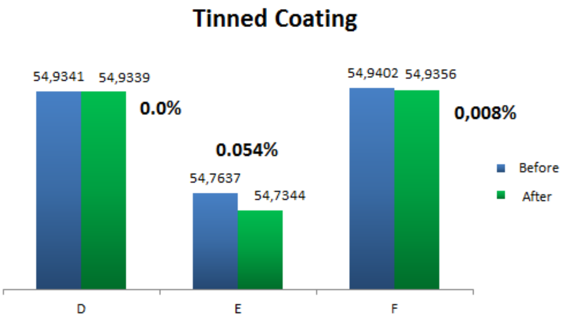


Figure 4: Ethanol Images Before and After 26 Weeks cycle.

To analyze visually, it can be noted that the ethanol contained in the specimen coated with tin coating after the test showed varying color, becoming milky, which did not occur with Ethanol organometallic coating. Thus, it can be said that the body of evidence that had tin coating was migrating some of its elements for fuel.

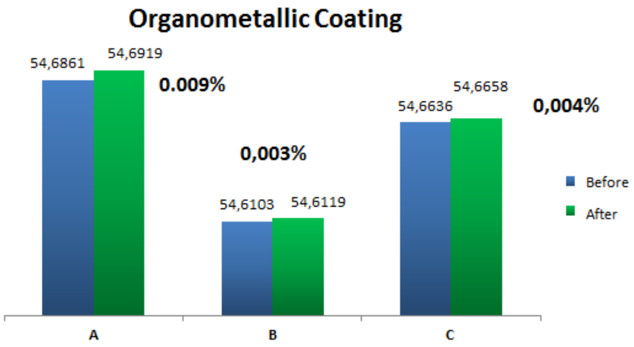
MASS LOSS

Through the mass change, it the initial mass difference and final mass, it was possible to evaluate the characteristics of each coating. Taking as basis weight variation that is the ratio of the final weight minus the initial soon positive and negative values refer to weight gain and loss, respectively. Chart 1 and 2, observed loss / weight gain in the bodies of tests performed in triplicate of the tin coating. Taking as basis weight variation that is the ratio of the final weight minus the initial soon positive and negative values refer to weight gain and loss, respectively. In Table 1, it was possible to observe the loss in weight in the test samples made of the tin coating in triplicate.
For the tin coating, Graphic (1) confirms - if the mass loss occurred in two of the samples, and it is also possible to observe that the mass loss with great significance was the test Body F with 0.054% loss.
For assessment of weight loss in test specimens made it was verified that D cup had no noticeable mass variation, and the visual assessment of the three specimens D was the only Sample beaker which was not this oxidation can identify some point in the casing.



Graph 1 - Coating Mass Loss Tinned

Through the Graph (2), the variation was observed masses. Instead of losing, the specimens won masses amounts of low significance, namely the house of thousandths of a gram, namely with variations of similar gains.

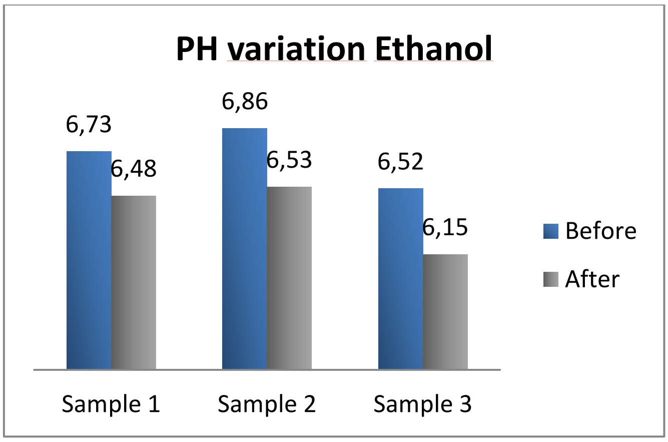


Graphic 2 - Mass Gain Organometallic coating

The probable cause of weight gain is the possibility to form the coating alloy of zinc and aluminum oxides, which are the main metals used for forming the organometallic coating.

PH MEASUREMENT

This parameter is measured to analyze the ethanol oxidation potential. Thus, the smaller the value of pH is more conducive to the plates undergo oxidation action through Ethanol solvent. Figure 3 shows the average values of pH of ethanol before and after the test period, respectively.



Graph 3 - Average pH values before and after the test in 26 weeks in proof tin coating body.

Even with little variation in the results, it was noted that the pH of the initial Ethanol showed neutral pH versus pH after the test, but this difference was not enough to prove that the corrosion on test specimens interfere in the composition in ethanol. It was also possible to notice that the pH was not instrumental in the development of corrosion, since the values obtained were almost neutral pH and ranged between them.

Scanning Electron Microscope (SEM)

Figures 5, 6 and 7 represent the images obtained by SEM, with a magnification of 250 to 1000 times, the residue ethanol from the specimen with tin coating, which showed corrosion.

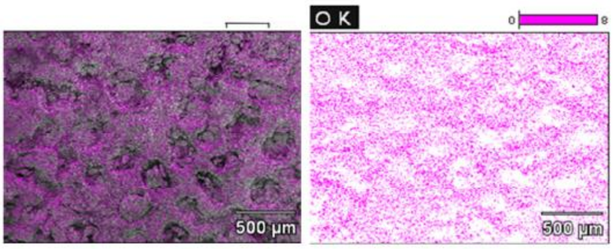


Figure 5 - micrographs obtained by SEM - Scanning the area with the presence of O.

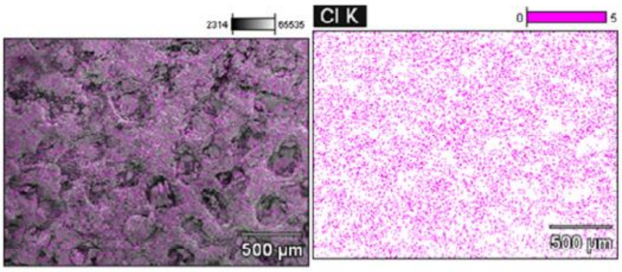


Figure 6 - SEM micrograph pbtida - scan the area with the presence of Cl.

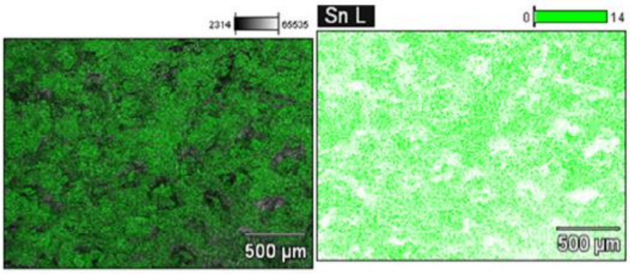


Figure 7 - micrographs obtained by SEM - Region scan with the presence of Sn.

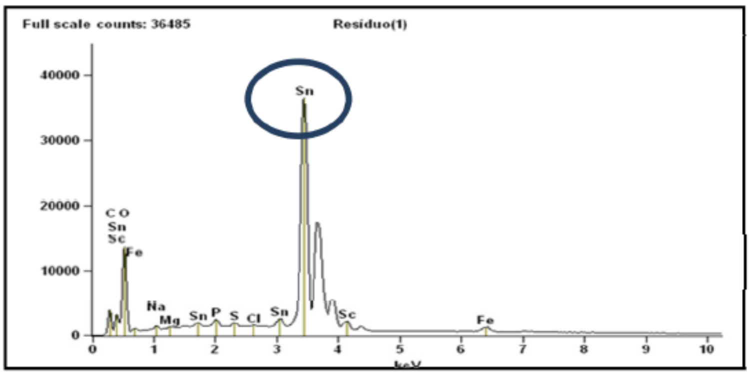


Figure 8 - EDS analysis on the ethanol residue

Looking at Figure 5, one can verify the presence of oxygen, which are the oxides formed by metals present in the coating surface. Through varregura performed (Figure 6), which corresponds to the chlorine element is observed that in all regions predominated this element, which proves the predominant impurities in the ethanol fuel. According to KURI and Ambrozin describe that one of the potential that can cause worsening of corrosion in plates is the presence of chlorine in ethanol, significantly increasing the corrosion process of steel sheet, and are associated will high conductivity and low pH fuel.

In Figure 7, one can verify the presence of tin considered to be most important element, since its presence proves that the sample with the tin coating underwent a type of corrosion, resulting in contamination of ethanol. Through the analysis by EDS, it was possible to prove semiquantitatively the prevalence of tin in ethanol residue in the test piece tin coating.

It was observed on all pictures made by EDS, the tin coating suffered corrosion, noting that the organometallic coating is more resistant to corrosion, knowing that the prevention of the corroão is an important factor to be cosiderado during product design. In some cases, the resistance to corrosion is a dominant factor in the selection of the material or process to be applied to an automobile.

3. CONCLUSIONS

This study analyzed the effect of corrosion in the fuel ethanol in organometallic and tin coatings, simulating the fuel tank surface. It was held from successful way in residue analysis of fuel ethanol and coatings, which revealed the presence of corrosion on the test piece tin coating and the presence predominating tin element in the waste of fuel, which proves the function of corrosion the impurities in the ethanol fuel.

The fact that the percentage change in weight loss demonstrates the general corrosion on the coated surface, which could not be identified in the measured pH, a key factor in the corrosion process studied, since the values obtained were practically neutral pH and non- They varied greatly during testing. The images obtained from SEM associated with semi-quantitative chemical data of EDS, allowed a better understanding and description of the presence of impurities in ethanol as chlorine and water, and the presence of the element from the tin corrosion process. Thus, the SEM images collaborated with visual observations already verified, where it was shown that samples with tin coating were conducive to corrosive attack while samples that had the organometallic coating did not suffer corrosion.

Through the results presented, it is concluded that the ethanol fuel is contaminated by the effect of corrosion on tin coating, which may cause obstruction in the fuel filter that is intended to retain all the impurities circulating in the power system and also in other components of the engine.

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