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**EFFECTIVENESS OF ENVIROFUELS
LUBRICATION TECHNOLOGY PACKAGE**

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PATENTED TECHNOLOGY » PROVEN RESULTS » PAYBACK

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This document is a summary of the research, development and testing performed by us on EnviroFuels, LLC (EnviroFuels) EF-200 lubricant additives that have been demonstrated effective in increasing fuel efficiency and reducing environmentally damaging emissions accompanying combustion of petroleum fuels in internal combustion engines. This research has provided a better understanding of the effects of EF-200 and the underlying mechanisms, leading to the improvement of the formulation, and providing a basis for successful field tests of their performance. While this paper is necessarily technical, we attempt to address an audience with a general scientific or engineering background.

INTRODUCTION

The acquisition in 2002 by EnviroFuels, L.P. of technology developed by MDEChem was based upon impressive tests of energy efficiency and emissions reduction due to, according to U.S. Patent 5,540,788, the formation of iron-phosphate conversion surfaces through contact of the metal surface with the additive formulation in oil.

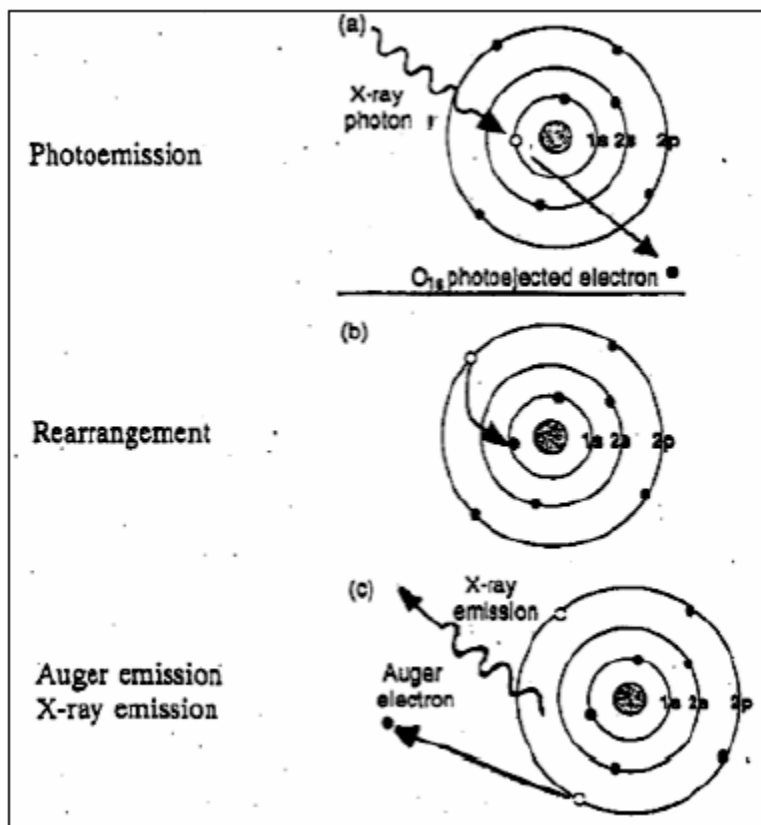
LUBRICANT APPLICATIONS

Accelerated testing, involving contact of metal alloy surfaces with both the aqueous and final product (oil) phases at concentrations of phosphate higher than used in product formulations, was employed to avoid long time periods required to observe surface effects. The treated surfaces, following removal of excess treatment fluid, were subjected to a suite of state-of-the-art analytical instrumentation for measurement of surfaces. Included among these were Auger, X-ray photoelectron (XPS, ESCA), and X-ray fluorescence (XRF, EDS) spectroscopies, the principles of which are diagrammed in *Figure 1*.

Other techniques employed in defining the surfaces were optical and scanning electron (SEM) microscopies, infrared spectroscopy with diffuse reflectance (FTIR/DRIFT), low angle X-ray diffraction, and some chemical testing as well.

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Figure 1



Conditions of treatment of the metal alloys included brief direct contact of the aqueous phase product at temperatures from ambient to engine temperature (180°F), and for longer periods with the oil/dispersant product containing 0.3% w/w P at 180°F. Surface analyses were performed either at Rocky Mountain Laboratories (Golden, CO) or in our laboratories.

Fe Alloy Surfaces

Experiments were conducted with polished 1018 steel, an alloy containing minor amounts (<1%) of C, Mn, Si, and Cu, and trace amounts (<0.1%) of P, S, Mo, and Sn, with Fe content of 98.4%. The result of the treatment with EF-200, is shown in **Figure 2** which consists of high resolution SEM micrographs of the blank and treated surfaces. The difference in texture of the surfaces is apparent. Auger spectroscopy profiles of these two surfaces are shown in **Figure 3**. The Auger profile of the polished steel (blank) surface reveals a thin oxide film of about 10 Å thickness, a typical value for an air-oxidized steel surface. (The thin layer of C, about 5 Å, is adventitious surface carbonaceous material adsorbed from the air that is present on all samples exposed in even the cleanest environment. (It is difficult and unnecessary to remove for this analysis.) The surface treated with EF-200 shows an oxygen-containing conversion surface about 120 Å in thickness, and containing a maximum O content at 60 Å, with small amounts of P and N at about 20 Å. The O profile is interpreted as due to PO_4 formation at the surface.

Figure 2

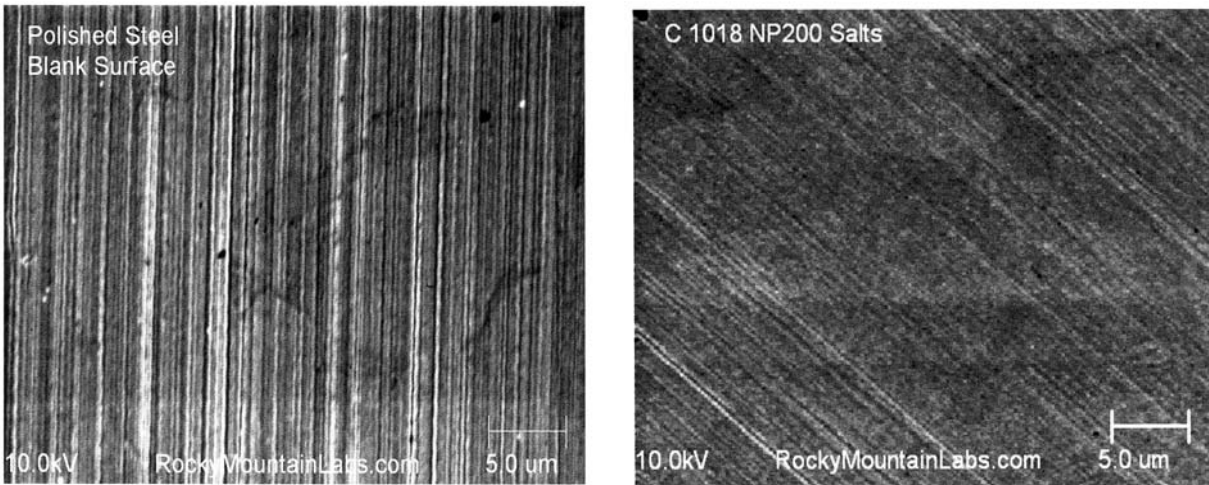
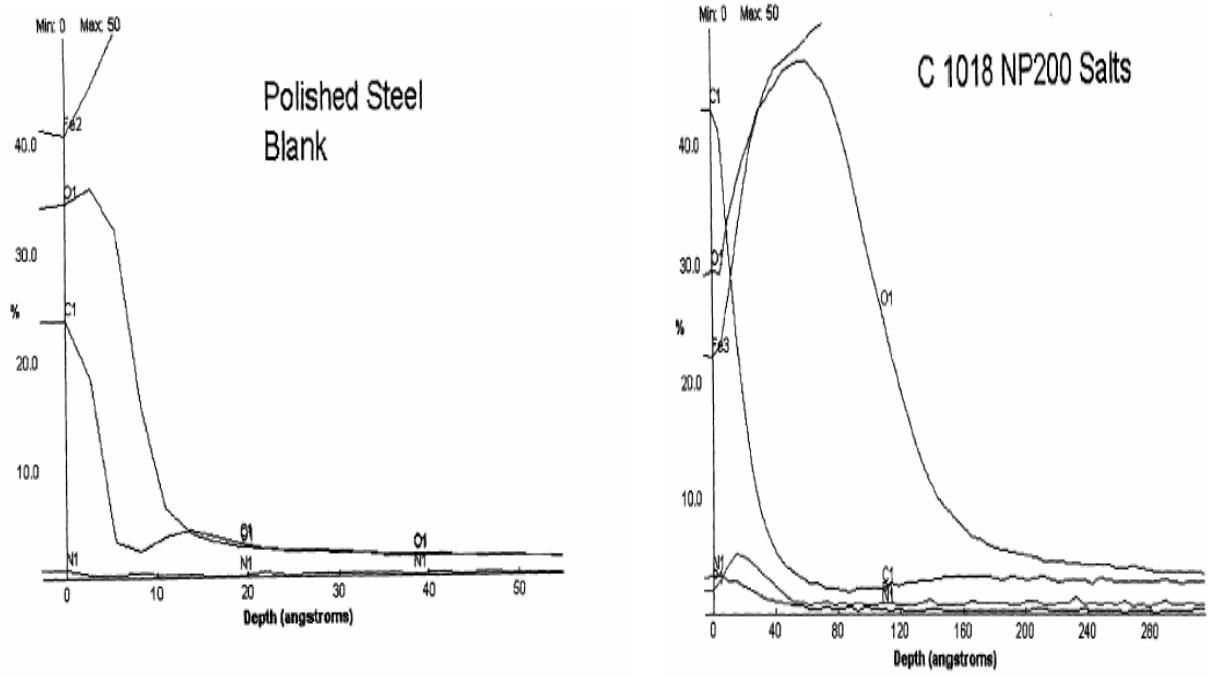


Figure 3



X-ray photoelectron spectroscopy (XPS) or electron spectroscopy for chemical analysis (ESCA) also was performed on these samples. The results are shown in **Figures 4-6**, revealing (**Figure 4**) the presence of P, K and N in the conversion surface. (The sensitivities of element detection in this technique differ greatly and the relative heights of the small peaks in the XPS spectrum are not indicative of the concentrations of the detected species.) Curve resolution of the expanded peaks for Fe and P (**Figures 5 and 6**, respectively) yield information on the nature of the surface species. The iron oxide in the conversion surface appears to be a mixture of Fe₂O₃, FeOOH and FeO, while the P is oxidized and present as phosphate in the form of PO₄³⁻ and P₂O₇⁴⁻.

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Figure 6

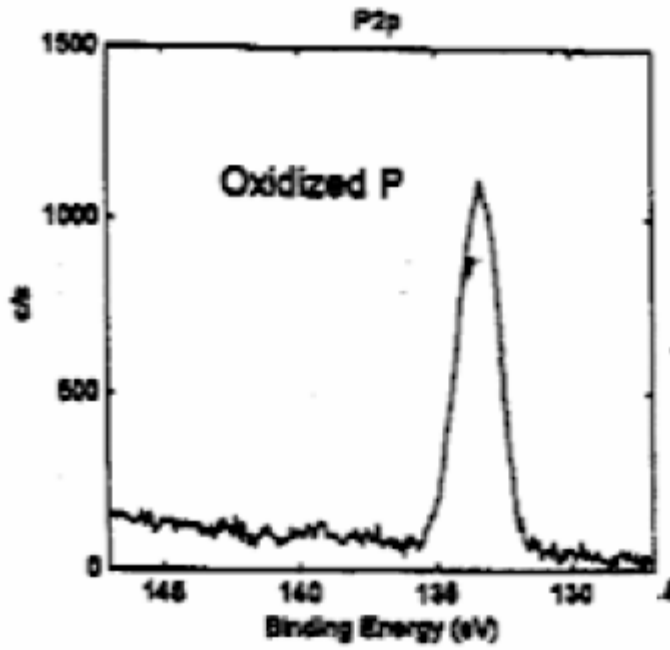
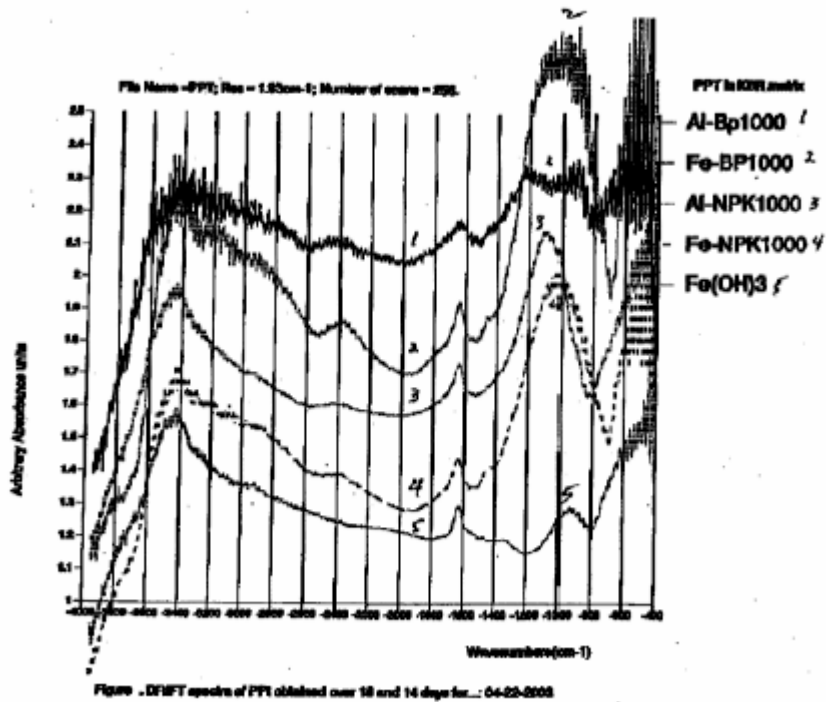
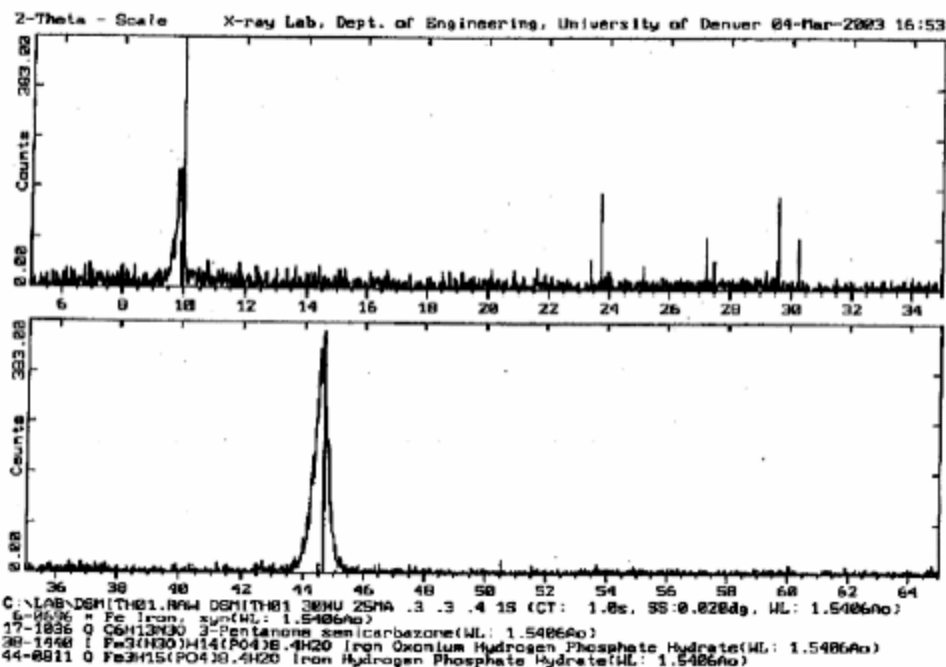


Figure 7



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Figure 8



Fourier transform infrared (FTIR) spectroscopy was performed on 1018 steel cylinders exposed to the aqueous parent solutions, utilizing a diffuse reflectance (DRIFT) attachment. Several spectra, including those of the steel surface, are shown in *Figure* and indicate the presence of iron orthophosphate with hydrated iron oxide. Low angle X-ray analysis also was used to examine this conversion surface, and the surface had enough long range order in this case to produce an interpretable pattern. The X-ray pattern is *Figure 8* and reveals the presence of hydrated iron orthophosphate, elegantly confirming the interpretation of the previous analyses. In summary, the nature of the conversion surface on steel produced by the active components of EF-200, prepared from the aqueous parent solution, is that of a variable composition metal phosphate. Depending upon surface location and operating conditions, this conversion surface ranges from simple FePO₄ to more complex phosphates such as Fe₃(H₃O)H₁₄(PO₄)₈·4H₂O, KFe₂[HPO₄]₂PO₄, NH₄Fe₂[PO₄]₂, etc., and related compounds including condensed phosphates such as pyrophosphate, P₂O₇⁴⁻, as examples. Coordination of the phosphate structure to the metal (Fe) ions in the surface conversion layer, typically the tetrahedral phosphate sharing edges with the oxygen atoms of octahedral iron oxide, undoubtedly is the origin of stability of these surface compounds. Potassium and ammonium ions in the interstices of the structure also are stabilizing.

Our interpretations of the surface analyses are consistent with known chemistry, as these compounds can be prepared separately as layered structures, stable at high temperatures, by hydrothermal reactions in the laboratory.

Thus, based upon the experimental evidence reviewed here, electron spectroscopies (Auger, XPS, and SEM), infrared spectroscopy (FTIR/DRIFT), low angle X-ray diffraction, and chemical evidence, the complex iron phosphate surfaces appear to be the result of the reaction of dihydrogen and monohydrogen orthophosphates reacting with both metal and metal oxide sites at

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elevated temperatures. This chemistry, simplified, can be summarized by a composite reaction such as the following, using only representative surface reactant and product species.



Chemical tests performed in our laboratory confirm the evolution of hydrogen from direct contact of the aqueous phase with the steel alloy as well as the increase of solution pH with time, both of which occur concomitantly with such a surface reaction.

Al Alloy Surfaces

Although the reaction between the aluminum surface and the aqueous phase component of EF-200 is less vigorous than that between steel and these reagents, no doubt due to the more impermeable natural oxide layer on the metal, the surface does produce a complex phosphate layer similar to that described for steel. **Figure 7**, the FTIR/DRIFT spectra of the metal surfaces, shows the result of treatment of 1100 Al alloy with the aqueous components of the product. Both spectra indicate the presence of an aluminum phosphate structure. The Auger spectra and profile of the Al alloy surface following treatment, **Figures 9 and 10** respectively, reveal the presence of a small amount of N, sizable concentrations of K and P, and a conversion layer depth of about 80 Å with the O content going through a maximum due to surface PO₄.

Figure 9

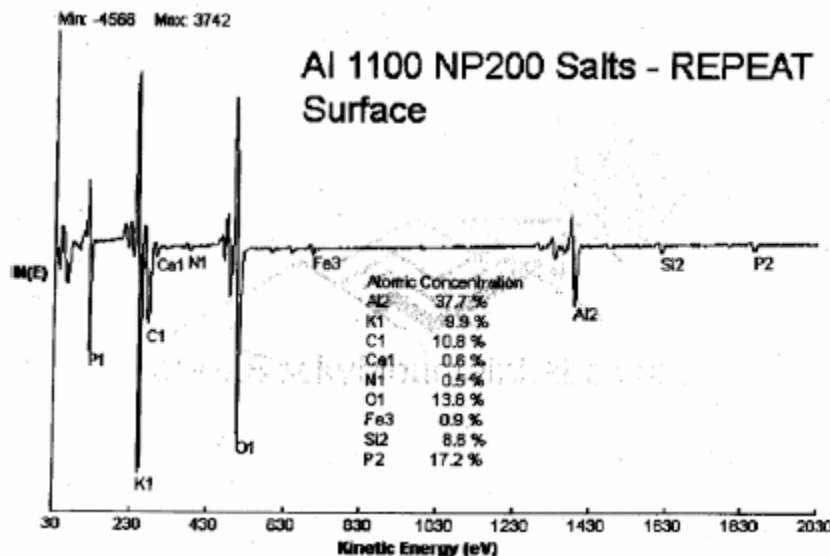
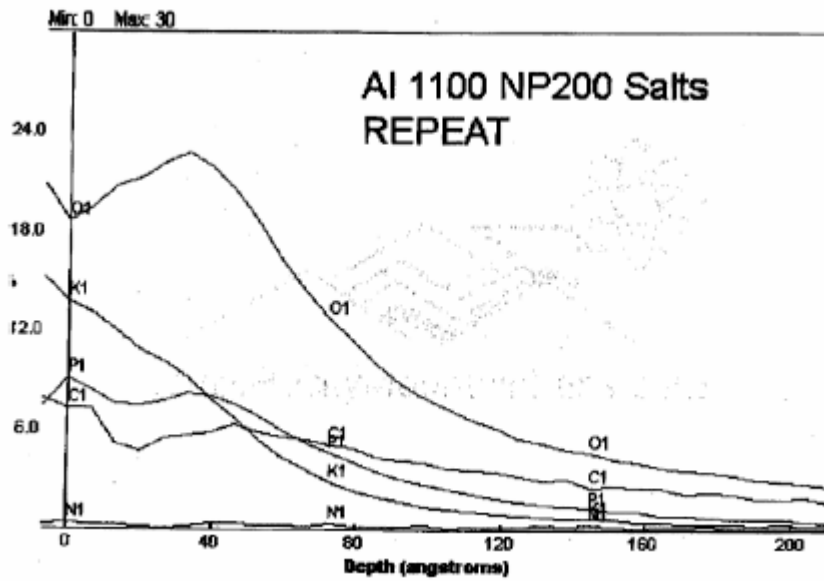
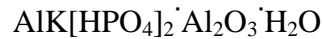


Figure 10

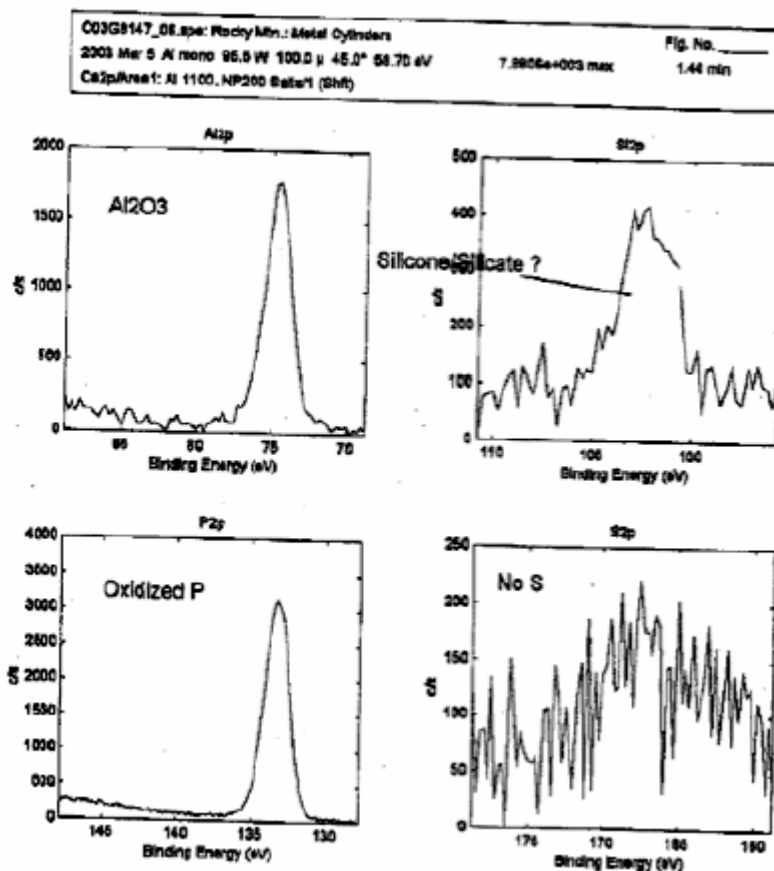


The XPS (ESCA) spectrum and resolution of expanded peaks, **Figures 11 and 12** respectively, reveal the presence of N, K and P in the conversion surface, with the Al as Al_2O_3 and the phosphorus as PO_4 . These analyses indicate the same phenomenon observed with steel after contact with the product components, a surface conversion layer that appears to have an average empirical formula such as



although no doubt of variable composition including the simple AlPO_4 depending upon the surface site and treatment conditions.

Figure 12



Laboratory tests in this case also indicate a chemical interaction represented by a composite reaction such as



Evolution of H₂ is observed upon contact of the surface with the aqueous component and the solution pH increases with time as in the case of steel. It appears, in the Al case, that the surface conversion layer is somewhat less complex than that with steel and that mostly K⁺ is held within the layer for stabilization.

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