A Compatibility Study of FEFO With Various Containment Materials

Timothy J. Shepodd, Steven H. Goods, Sandia National Laboratories, Livermore, CA 94551-0969.
Patricia Foster, Mason & Hanger Pantex Plant, Amarillo, TX 79177.

Abstract

We report on a program to evaluate the compatibility of energetic fluids with candidate containment materials. The energetic fluids are constituents of various extrudable explosives. The paste-like explosives consist of explosive particulates (HMX, TATB for example) suspended in the energetic liquids and are designed to remain extrudable over a wide temperature range for many years. Any interactions between the transferable paste and the containment materials could change the composition, viscosity, initiation or energetics of the explosive as well as cause failure of the containment vessel.

One of the paste formulations of interest consists of fine particulate triaminotrinitrobenzene (TATB) and fluid bis-(2-fluoro-2,2-dinitroethyl) formal (FEFO) with small additions of polymer viscosity additives. Compatibility between FEFO and a number of organic and metallic materials has been evaluated. The metals included common structural alloys and elemental metals that the extrudable explosive might contact in its service life. The organic materials included flexible materials for use as collapsable extrusion membranes or permeation barriers, rigid engineering resins which might be used as matrices for composite structural vessels, and the polymer viscosity modifiers used in the final formulation. Materials were exposed to the FEFO at 22 and 74°C for up to eight months. Changes in weight, appearance, and mechanical properties (polymers only) were measured. Surface corrosion products were characterized using electron dispersive spectroscopy, Auger analysis and X-ray photoelectron spectroscopy. The FEFO was analyzed for dissolved impurities that could have come from the exposed materials as well as changes in its chemical composition. FEFO/material interactions were also evaluated in a permeation study that measured kinetic and thermodynamic parameters for the uptake of FEFO into various Teflon® and polyethylene materials.[1] The effects of these exposures to FEFO are compared to material exposures in the explosive paste itself. In this way we can assess if exposure in neat FEFO constituted an accelerated aging test relative to exposure in the actual paste. Further, the results from these exposures to neat FEFO will be compared to earlier studies of liquid explosive mixtures containing FEFO.[2]

304 stainless steel, Al 6061-T6, and Monel 400 showed evidence of surface attack (oxidation or pitting) after ≈ 100 days of exposure. XPS analysis revealed that the gold reacted to form gold cyanide. The platinum, iridium, titanium, tantalum, Ta-10% W showed little or no evidence of reaction. Generally, neat FEFO was shown to be substantially less agressive to most metallic materials than the mixed liquid composition perviously studied.

Among the organic materials, the per-fluorinated materials showed only slight interaction with the FEFO while the polyethylene, polyester and Aclar® materials were changed by the FEFO. These changes were manifested in changes in color, net weight gain, and small changes in mechanical properties.

Introduction

The use of transferable paste explosives requires the qualification of containment materials for long-term exposure. Either organic or metallic materials may be used in a containment or transfer system. Metallic materials can be used for the main structural components while organic materials can be used for permeation barriers and flexible structures such as bladders, membranes, and seals. Previously, we have tested a mixture of the liquid components of a paste explosive (RX-08-FK)[3] against an extensive matrix of materials.[2] These liquids were found to be very aggressive towards many metallic and organic materials. In the present study, we investigate material compatibility with a new formulation developed by Lawrence Livermore Laboratory which is based on TATB, an insensitive solid explosive. The composition of this paste, designated as RX-52-AE, is : TATB, 65.0 wt.%; FEFO, 32.0 wt.%; polyvinyl formal, 1.6 wt.%; polycaprolactone diol, 1.4 wt.%. The fluid carrier is FEFO and small amounts of dissolved polymer viscosity modifiers. The choice of metallic and organic materials selected for FEFO exposure was aided by the earlier study in which many materials were found to perform unsatisfactorily when exposed to the mixture of energetic liquids. Since one of the liquids in that mixture was FEFO, few of those materials were included in the present work.

Experimental

FEFO

The FEFO (a hazard class 1.1 mass detonating, high explosive) was supplied as a 30-35 % solution in ethyl acetate. The material was manufactured in 1971 by Rocketdyne, and has been stored since in closed, polyethylene-lined containers under uncontrolled conditions (temperature, humidity, etc.). The diluted FEFO was stripped of ethyl acetate first on a rotary evaporator then under vacuum. Because of the age and the unknown history of the FEFO, it was stirred with ≈ 10 wt. % activated carbon and filtered. The carbon filtration was repeated. The carbon filtration caused the color of the FEFO to lighten from a deep yellow to a straw color. Analysis by gas chromatography of the purified material showed traces of higher molecular weight materials (probably isomeric and polymeric formals) as the only detectable impurities. Trace element analysis (ICP-MS) of the FEFO impurities showed only aluminum, silicon, and calcium present at >1 ppm. Chlorine was not detected at the detection limit of 2 ppm.

Metals

Several elemental metals were chosen for study: gold, platinum, iridium and tantalum. In addition a number of corrosion resistant alloys were examined: Monel 400, aluminum 6061, Ta-10%W, titanium-Grade 12, and two stainless steels: 304 SS and 21-6-9. Corrosion coupons measuring 6 mm x 25 mm were machined from these materials. All of the metal coupons were polished to a 0.1 μm finish using standard metallographic techniques. In addition, gold foils (0.05 mm x 2 cm x 5 cm) were placed in exposure to maximize the surface area in contact with the FEFO so that any reaction in terms of surface films, weight changes, and dissolved metal would be evident.

Organics

The organic materials chosen for exposure were: polyethylene; PET polyester; Aclar 22C; a graphite epoxy composite; two vinyl ester thermoset resins: Derakane 47-36 and Derakane 8084; and five Teflons: PTFE, FEP, PFA, and Kalrez (carbon-black-filled Compound 4079 and unfilled Compound 1045). Also, samples of 0.254 mm PFA Teflon plated on 1 side with metal (one set with gold and one with aluminum) were placed into exposure. All organic materials had tensile bars in exposure. All of the membrane materials also had witness coupons and a large coupon for weight change analysis.

Exposures

All exposures were performed at the Mason and Hanger, Pantex Plant, Amarillo TX. All specimens were submerged in FEFO in borosilicate glass vials. However, duplicate sets of the gold coupons were exposed in PTFE Teflon vials. The uncapped vials were arranged in PTFE Teflon racks and placed into gold plated stainless steel canisters. The canisters were sealed with an aluminum gasket and degassed with repeated evacuation cycles to 20-50 torr refilling each time with helium. The exposures were performed under ≈ 500 torr of helium. One canister was aged in a 74 °C oven, the other was aged at room temperature (21 ± 2 °C). Periodically, samples were removed for observation and weight change analysis. Twice during the test, half of the tensile samples were removed for mechanical properties analysis.

Results

Metals

None of the elemental metals (except for gold) showed any obvious signs of interaction with FEFO at either room temperature or 74 °C. The titanium and Ta-10%W alloys also exhibited good corrosion resistance at both temperatures. Below we summarize specific observations regarding the interaction of FEFO with the less compatible metallic materials. Except for the gold and Monel exposures, trace metals analysis of the FEFO (ICP-MS) failed to identify the metals above the concentrations found in control samples. In most of these cases 50 ppb of dissolved metal would have been an obvious spike above background and control.

Stainless steels

The 304 stainless steel showed clear evidence of attack. Corrosion was evident after 55 days of exposure at 74 °C, and after 125 days at room temperature. The specimens developed discrete 1.0 – 2.0 mm diameter areas of corrosion surrounded by unblemished metal. Extensive pitting was associated with each corrosion feature. The morphology of these corrosion features is shown in Figure 1a, a scanning electron micrograph

which suggests that the pitting was crystallographic in nature. Much of the metallic corrosion products easily washed off when the specimens were rinsed clean of FEFO. Indeed, most of the corroded or attacked areas on the steel samples showed no remaining corrosion products as determined by energy dispersive x-ray spectroscopy (EDS). Spectra obtained from previous studies of steels exposed to similar liquids indicated only the presence of the principal alloying elements of stainless steel – Fe, Cr and Ni.[2] In that instance, EDS analysis revealed an oxygen peak, consistent with the presence of an oxide.

EDS reveals that there were silicon-base deposits surrounding these pits. These deposits result from the dissolution of the borosilicate vials by the FEFO.[2] This dissolution of the glass and its re-deposition occurred on many of metallic coupons and was especially severe at the elevated temperature.

The 21-6-9 immersed in FEFO at 74 °C also showed signs of attack after 55 days of exposure. The corrosion products had a rust color, which is consistent with an iron-based oxide. The coupon exposed to FEFO at room temperature was somewhat less attacked after 55 days but was clearly oxidized after 125 days of exposure.

Analysis of the FEFO in which these coupons were exposed (using ICP-MS) did not reveal the metallic constituents of the steel, indicating that these products were insoluble in the liquid. However, the residual corrosion products had a rust color, which is consistent with an iron-based oxide. Regardless of the precise corrosion mechanism or products formed, the 300 series stainless steels are clearly unsuitable for use as long-term containment materials.

Monel

The monel coupon exposed at 74 °C exhibited visual evidence of corrosion after 125 days. An SEM micrograph (Figure 1b) reveals the presence of crystallographic pitting. The attack appears to be identical to that observed in the earlier study[2] in which this pitting was preceded by surface blistering. With increasing exposure time, the polished metal surface became cloudy. EDS analysis showed only the principal alloying elements (on both the blistered surfaces or within the pitted regions).

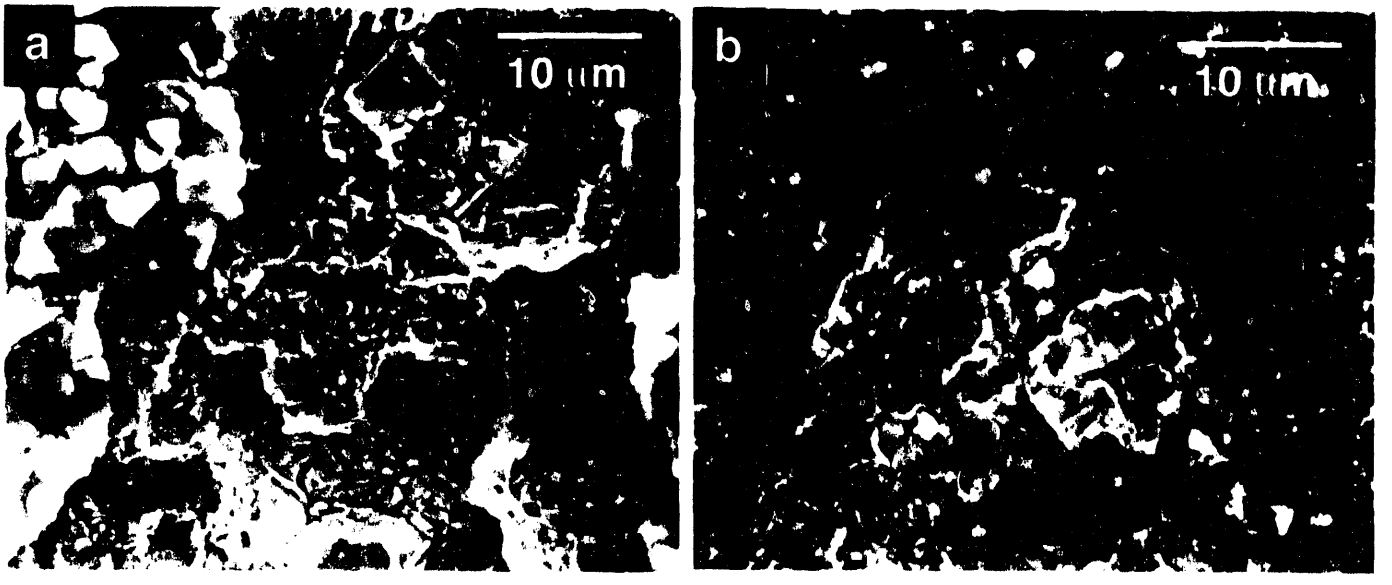

Figure 1. (a) Scanning electron micrograph of 304 stainless steel surface reveals presence of extensive pitting . Silica deposits result from the dissolution of the glass containers. (b) Monel exhibits extensive pitting resulting from the spallation of surface blisters.

Aluminum

At room temperature the most prominant response of the 6061 alloy was the formation of a silica film from the dissolution and re-deposition of the of the glass vial that completely covered the specimen surfaces. This film ranged in thickness from a few tenths of microns to approximately 4 microns. At 74 °C the silica was less uniform and formed irregularly shaped deposits. There was some evidence of pitting after exposure at 74 °C for 227 days. However, this pitting was minor compared to that which occurred in the stainless steels after comparable (or even much shorter) times.

Gold

The gold specimens developed an obvious, but uneven, tarnish film after 55 days of exposure at 74 °C and after 159 days at room temperature. XPS analysis of gold exposed under similar conditions reveals that this surface film results from the formation of gold cyanide.[4] This reaction is of great interest because of the usual inert nature of gold when exposed to aggressive media. The reactions between FEFO and gold have been studied in detail and are the subject of a separate paper at this symposium.[5] While gold does form reaction products with FEFO, the extent of those reactions appears to be small. With further study, gold may be suitable for use as an electroplated barrier in conjunction with conventional, but FEFO-incompatible, alloys.

Organics

Vials containing only FEFO were placed in exposure along with the material coupons. After 227 days, the room temperature control was unchanged while the FEFO at 74 °C yellowed slightly. The various organic materials showed different degrees of degradation after exposure. All the organic materials showed the presence of FEFO by infra-red spectroscopy. All Teflon and polyester samples showed no visible changes after exposure at either temperature. The polyethylene and Aclar 22C samples exposed at room temperature appeared unchanged, while the ones aged at 74 °C yellowed after 227 days. The larger Aclar 22C samples used for weight change measurements were rolled to fit into the vials. These samples developed stress cracks perpendicular to the curl. The two Derakane formulations, 470-36 and 8084, both showed some effects upon exposure that were accelerated at the higher temperature. The 8084 formulation developed slight surface crazing after 159 days. The FEFO surrounding the 8084 darkened to an orange color. The 470-36 formulation showed similar surface crazing and deep cracks. The FEFO exposed to the 470-36 became a dark brown. The graphite epoxy samples appeared unchanged. The FEFO exposed to the graphite epoxy sample at 74 °C was slightly more yellow than the control. Though the color changes of the samples and surrounding FEFO indicate some reactions are occuring, no differences in the chemical composition of the FEFO were noted by either NMR or GC/MS. 1000Å thick layers of aluminum and gold were sputter deposited onto PFA Teflon films and then exposed to FEFO. This film was a commercially available material that had been corona discharge treated to promote adhesion. The coating was opaque and remained adhered through standard tape tests. Upon an exposure of 68 days to FEFO these laminates degraded, especially at 74 °C. The aluminum had sloughed off the plastic in places, and the remaining metal was easily wiped off. The gold laminate showed small areas where the gold was gone, but also a uniform thinning of the metal to a transparent layer. This effect was more apparent at the edges suggesting that the FEFO also reacted with the gold by infilitrating the plastic/metal interface. Again the metal could be easily wiped from the Teflon. Though the failure of these laminates limits their usefulness in future engineered structures, the use of thin sputtered films (on an impervious metal substrate) may be useful for observing slow attack of the fluids on different metals.

Viscosity Modifiers

Two polymers are dissolved in FEFO to control viscosity in RX-52-AE. Their compatibility was tested by aging them each with FEFO in deutero-1,1,2,2-tetrachloroethane solution, at 74 °C, for 250 days. Control samples without FEFO were aged under the same conditions. The samples were removed periodically from the oven and their GC/MS, ^{1}H and ^{13}C NMR spectra were recorded. The polycaprolactone diol (Tone 240, Union Carbide) showed slightly different NMR spectra with increasing aging time. Tone 240 is a diol initiated polycaprolactone that can rearrange under acid or base catalysis. GC/MS traces of the aged mixture revealed no new volitile products of consequence (≤ 250 °C). We assume that the changes involve the terminal hydroxyls reacting with ester sites along the backbone, thus changing the molecular weight distribution of the polycaprolactone without seriously degrading the performance of the polymer. The polyvinylformal (Formvar 5/95E, Monsanto) showed almost no indication of any reaction with FEFO by NMR or GC/MS.

Weight change measurements

Weight changes of the polymers as a function of time were examined as a quantitative measure of the interaction of the organic materials with the liquid. Figure 2 shows the results of these measurements for coupons exposed at 74°C. Due to the limitations of the balance used, weight changes of less than 0.05% were not considered reliable. Only those materials that exhibited significant weight changes are shown in Figure 2. While weight changes of only a few percent are not necessarily indicative of fundemental incompatibility, it does suggest that further assessments are necessary before a material can be qualified for prolonged exposure. The weight change of the polyester coupon at 74 °C exhibited a parabolic time dependence suggesting a diffusion controlled, self-limiting process.[1] Compound 1045 showed markedly larger weight change than Compound 4079. While it has inherently poorer mechanical properties than Compound 4079, it is chosen for its superior performance in severely oxidizing environments. Both Kalrez formulations appear adequate for the present application.

Weight change measurements of the organic specimens exposed at room temperature are not shown. At that temperature, only the polyester exhibited systematic increases in weight above the resolution of the balance. After 283 days of exposure the weight change of the polyester was ≈ 0.15%.

Mechanical properties

Mechanical properties were measured for the organic materials after 125 and 227 days of exposure. Duplicate or triplicate tests were run for each material. Figure 4 shows the change in fracture strain as a percentage of baseline ductility (for unexposed material) after the longest exposure period. Because of the limited number of specimens available for repeat testing, changes of less than 20% should not be considered significant. Although PTFE exhibited no significant weight change over the course of the experiment, the mechanical tests revealed a measurable increase in ductility suggesting that the dissolved FEFO plasticizes the polymer matrix. Only the polyester and Aclar exhibited significant ductility losses under these exposure conditions. Neither the Derakane resins nor the graphite-epoxy specimens are shown since their minimal ductility makes the kind of comparisons presented in Figure 4 unreliable. None of those materials exhibited any measurable changes in ductility or strength.

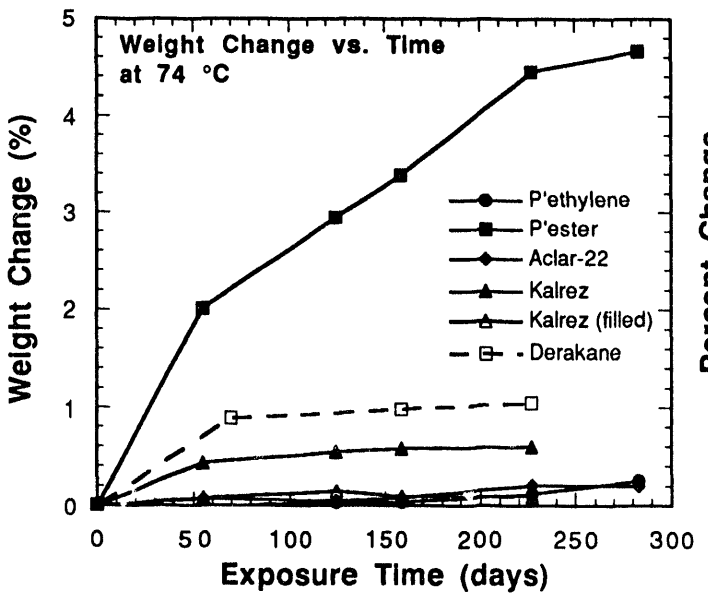

Figure 3. Weight change measurements for polymer specimens exposed at 74 °C to FEFO.

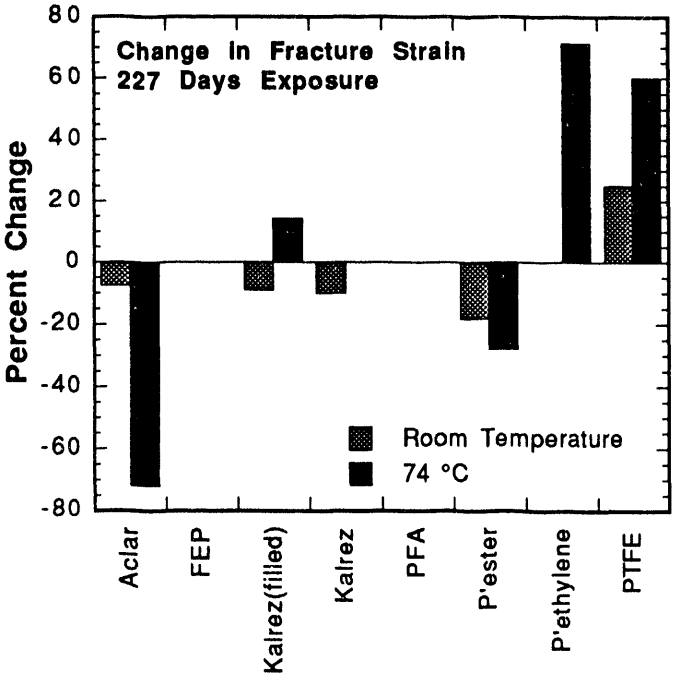

Figure 4. Change in fracture strain of organic specimens after 227 days of exposure to FEFO.

Conclusions

The stainless steels did not exhibit adequate compatibility for long-term exposure to a FEFO-based paste explosive. Oxidation appears to be the principal mechanism by which chemical attack occurs. The aluminum alloy showed some evidence of minor pitting at 74 °C. Monel 400 also proved to be an unacceptable containment material, exhibiting a tendency to blister and pit while exposed to FEFO. Although the gold showed some evidence of interaction with the liquid, the level of interaction with FEFO does not preclude it from use as an electroplated barrier. The rest of the alloys and elemental metals showed no evidence of degradation after exposure to FEFO at either temperature. The results presented here identify potentially compatible organic materials such as Kalrez, FEP, and PFA. None of these materials showed any visual, physical, or mechanical property changes after exposure. For ambient temperature applications, polyethylene and polyester may be adequate. The minimal reaction between the viscosity modifiers and FEFO suggests that RX-52-AE will not degrade over time.

At this writing, additional tests are in progress that address the issue of material compatibility for all of the liquid constituents of RX-08-FK. Many of the materials described here are included in this test matrix. In addition, many more organic materials are being examined.

Acknowledgment

We would like to thank: William Yoshimoto, George Buffleben, Bernie Bernal (SNL), Melissa Dodge, Bill Sims, Tim Quinlin, and Clifford Schaffer (Pantex) for their individual contributions to this effort.

This work is supported by DOE Contract # DE-AC04-94AL85000

References

[1]Shepodd, T. J.; Foster, P.; Daniel, A. R.; Buffleben, G. M. "The Permeation of FEFO, EDNP, ENP and 1,2,4-Trichlorobenzene Through Barrier Membranes". Submitted for publication; Sandia National Laboratories Report: 1993.

[2]Goods, S. H.; Shepodd, T. J.; Mills, B. E.; Foster, P. "A Materials Compatibility Study in FM-1, a Liquid Component of a Paste Extrudable Explosive, RX-08-FK"; Sandia National Laboratories Report: SAND93-8237 • UC-704, September 1993.

[3]von Holtz, E.; Scribner, K.; Whipple, R.; Carley, J. "Paste Extrudable Explosives. Their History and Their Current Status"; Lawrence Livermore National Laboratory Report: UCRL-LR-110156, Arpil 30,1992.

[4]Moddeman, W.; Sims, B.; Foster, P.; Goods, S.; Shepodd, T. Surface Spectroscopic Examinations of Gold and Aluminum Aged in FM-1/EDNP/EG Liqiuid Carrier for the PEX Program. Presented at the 18th DOE-Compatibility, Aging and Service Life Conference, Savannah River Technology Center, Aiken, South Carolina April 20-22, 1993.

[5]Moddeman, W.E.; Birkbeck, J. C.; Foster, P.; Goods, S.H.; Shepodd, T. J. Surface Analytical Studies of the Reactions of Platinum Group Metals with FEFO. Presented at the International Symposium on Energetic Materials Technology, Orlando, Florida March 21-24, 1994.

END

DATE
FILMED
3/8/94