Underwriters Laboratories Research Program on Material Compatibility and Test Protocols for E85 Dispensing Equipment

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Abstract

Fuel blends such as E85 comprised of gasoline and high percentages of ethyl alcohol (ethanol) are being deployed in the United States and other countries. The unique chemical nature of high-percentage ethanol fuel blends requires special consideration with respect to material compatibility. The polar nature of ethanol fuel may cause degradation of materials in contact with the fuel. This action may have the potential effect of increasing the likelihood of leaks from dispensing equipment or increasing the likelihood of other potential hazards. While fundamental comparative test methodologies have been developed for coupon level test samples, testing processes for dispensing equipment for high percentage ethanol fuel blends were not established. Underwriters Laboratories Inc. (UL) conducted a research program to define such processes.

The Need For Research

E85 is an automotive fuel blend of denatured ethanol and gasoline, nominally blended in the ratio of 85/15. E85 may be blended to include ethanol in the range of 70% to 90% based on seasonal blends, geographical blends, and quality control factors. E85 has been in use in the United States for use with specially designed flex fuel vehicles.

Traditional gasoline fuels, including low percentage ethanol fuel blends typically comprised of gasoline with up to 10% ethanol, have been in use for many years; products handling these fuels are addressed by established requirements. High-percentage ethanol fuel blends, with ethanol content above 15%, have different characteristics than traditional gasoline fuels. The polar nature of ethanol is significantly different from gasoline. Ethanol is significantly more conductive than gasoline and may increase electrochemical action. Ethanol's hygroscopic nature increases its propensity to absorb water. These different characteristics may result in a corresponding increase in degrading effects of ethanol fuel on materials in the fuel line.

Exposure of metallic parts to high-percentage ethanol fuel blends may result in degradation in the form of corrosion of metals, metal platings, or surface treatments, stress cracking, embrittlement, or fatigue. Additionally, the effects of galvanic interaction must be considered for high-percentage ethanol fuel blends such as E85. E85 is approximately a million times more conductive than gasoline. When exposed to E85, metals give up electrons, and the fuel serves as an electrical conductor. This galvanic interaction may lead to significant corrosion at dissimilar metal interfaces.

Exposure of nonmetallic parts to high-percentage ethanol fuel blends may result in degradation in the form of swelling, shrinkage, hardening, cracking, permeation, decomposition, solvation, or extraction. In particular, exposure to ethanol may cause significant increases in volume for some materials. Also, ethanol may strip strategic components such as plasticizers from nonmetallics.

These mechanisms of degradation to metallic and nonmetallic materials may in turn cause parts formed from these materials to subsequently fail to perform their safety function. In the case of dispensers, this could be primarily manifested in two ways. Degradation may result in loss of fuel containment, particularly for seals. Also, dispensers include parts providing necessary safety functions, to stop the flow of fuel under normal use conditions (such as valves) or abnormal conditions (such as breakaway couplings). Degradation may result in failure of a safety-related component to perform its safety function, which in turn may result in the risk of a fire or explosion hazard.

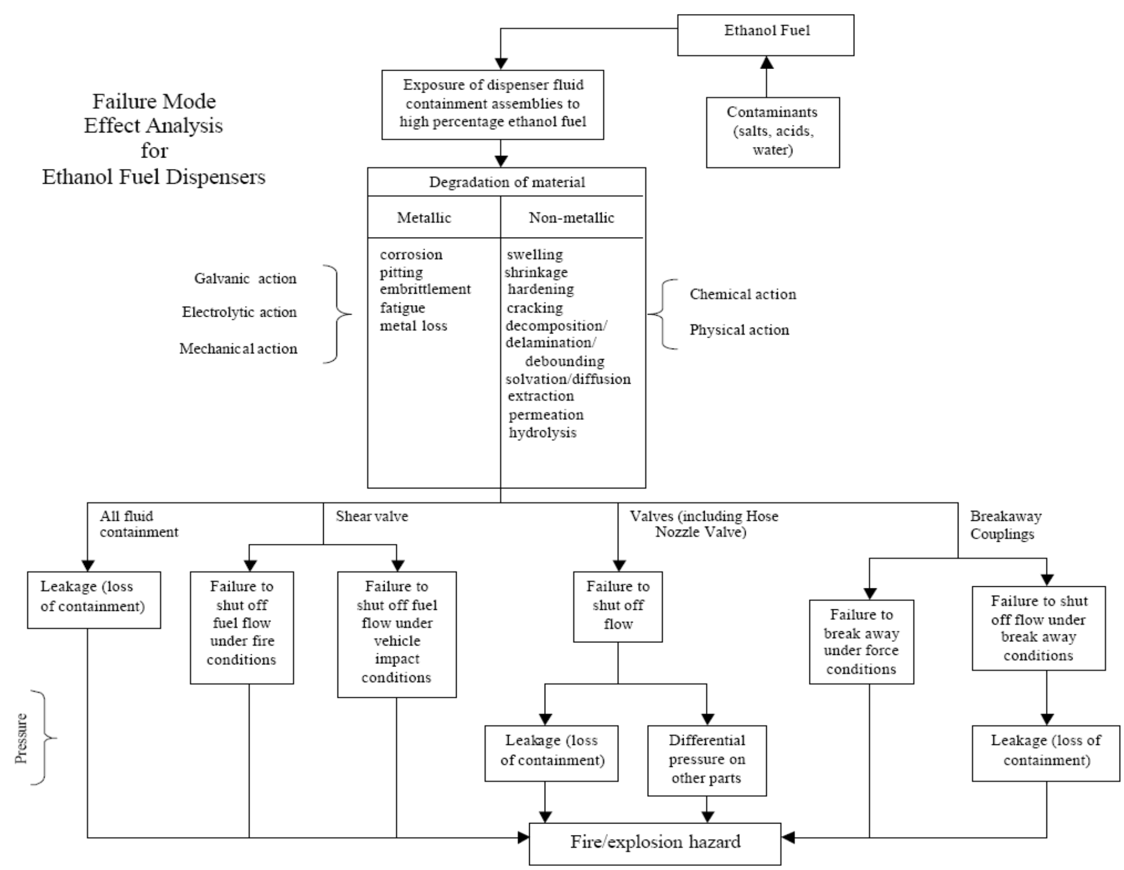

Figure 1 – Failure Mode Effect Analysis for Ethanol Fuel Dispensers

In reviewing the available technical information on the topic of material compatibility with high-percentage ethanol fuel blends, the technical substantiation for potential material responses to fuel exposure was established. However, neither specific technical information supporting the compatibility of particular materials nor applied scientific protocols to assess the effects of degradation on formed parts were available.

UL's objective was to define performance-based protocols that would permit the assessment of the safety of dispensing equipment, constructed from a variety of materials integrated into a particular design. In order to accomplish this, UL made the determination that there was a need to conduct research in order to identify appropriate material compatibility assessment protocols and requirements for E85 dispensers and dispenser components. The requirements would form a basis for assessing material response in the form of equipment safety performance. The requirements would address both minimizing the risk that exposure to high percentage ethanol fuel blends may ultimately lead to leakage of the fuel, and minimizing the risk of degradation that would result in the loss of a necessary dispenser safety function.

Research Overview

In order to develop foundational technical information for the safety requirements for E85 dispensers, the research test program included several elements:

- *Gasket and Seal Testing* – A test assessment of gasket and seal materials was initiated to gather data about the response of these materials to aggressive test fluids and to various conditions of exposure.

- *Conditioning Exposure Testing of Dispensing Equipment* – An exposure research test program was developed in order to assess response of formed parts to high-percentage ethanol fuel blends. This long-term exposure testing was performed at elevated temperature with the samples filled with defined aggressive test fluids.

- *Safety Performance Testing of Dispensing Equipment* - At the conclusion of the conditioning exposure, critical performance tests drawn from applicable UL standards were performed to assess fuel containment and safety performance, as applicable.

- *Analysis of Extracted Test Fluids* – Test fluids that had been extracted from the conditioning exposure test samples were subjected to analytical tests. The analytical tests identified extracted compounds and byproduct compounds of corrosion and degradation. The focus of these efforts was specifically to review the foreign compounds as they may affect the response of the dispensing equipment, and not fuel quality.

- *Harvested Product Assessments* – Samples of dispensers and dispenser subassemblies that had been in service in the United States and Brazil dispensing high-percentage ethanol fuel blends were obtained for evaluation. The dispensers and subassemblies were examined and subjected to particular relevant testing protocols in accordance with applicable UL standards for safety.

Test Fluids

Three seasonal blends of E85 are defined in ASTM D 5798, *Standard Specification for Fuel Ethanol (Ed75 – Ed85) for Automotive Spark-Ignition Engines*, published by ASTM International. Other high-percentage ethanol fuel blends, such as E20, are being used on a trial basis and considered for future use for all vehicles accepting gasoline.

Fuel blends over the range of ethanol/gasoline content have different properties. Ethanol/gasoline blends with higher gasoline content tend to be more degrading on nonmetallic materials, while blends with higher ethanol content tend to be more degrading on metals. However, both metals and nonmetals may show some response along the continuum. Experience from automotive and other applications indicates the most degradation tends to occur with blends having ethanol in the range of 25% (i.e. E25) and 85% (i.e. E85).

Potential fuel contaminants include water, salts, acids, and other substances. These contaminants may be introduced to the fuel at different points and subsequently passed along through the distribution chain, although the fuel station level appears to present the highest risk point for fuel contamination. Water may be present in storage tanks from sources such as condensation in atmospheric tanks, ground or surface water entering tank seals, settling out from petroleum products in previous use, and the like. Soluble road salts may also be present in surface water runoff and may end up in the fuel. Salt air condensation during sea transport or in coastal areas presents an additional risk of contamination from chloride compounds. Consideration of the fuel conductivity with absorbed water and salts is a key issue. Acids may also be introduced to the fuel during the production process, through oxidation of the fuel, or via surface water runoff. Using aggressive test fluids that include contaminants was identified as an important practical consideration.

Corrosion inhibitors are sometimes provided in high-percentage ethanol fuel blends. When provided, the inhibitors are included in extremely low concentrations – on the order of 30 lbs per 1000 barrels – to reduce the effects of corrosion on metallic parts in contact with the fuels. A high percentage of the E85 fuel produced today may include corrosion inhibitors, however inclusion of these inhibitors is not mandatory. The specific inhibitors used are not defined by regulations, and their corresponding efficacy is not known. As such, no reliance was placed on the effects of corrosion inhibitors in the research test program. However, as a part of the gasket and seal program the potential effects of inhibitors on these materials was considered.

Based on these considerations, tests with an E25 fluid and an E85 fluid to assess response of materials over the continuum of gasoline/ethanol blends were defined. The defined test fluids were identified as CE25a and CE85a for which:

- The “C” prefix indicates the use of Reference Fuel C as a standardized test fluid to represent gasoline; Fuel C is comprised of 50% isooctane and

50% toluene as defined in ASTM D 471, *Standard Test Method for Rubber Property – Affect Of Liquids*, published by ASTM International; and

- The “a” suffix indicates use of aggressive ethanol test fluid made through the introduction of defined amounts of water, sodium chloride, sulfuric acid and glacial acetic acid in accordance with SAE J1681, *Gasoline, Alcohol and Diesel Surrogates for Materials Testing* published by SAE International.

Time and temperature considerations

The time and temperature conditions necessary to establish the appropriate test conditions were carefully considered. In order to practically model performance of the dispensing equipment over a reasonable, extended period of time, the use of accelerants is necessary. Use of elevated temperature was identified as the most appropriate accelerant mechanism. The relationship between exposure time and exposure temperature is generally inverse. Elevation of the test temperature, based on the Arrhenius principle, will correspond to increased chemical interaction. Other testing methodologies for materials in contact with automotive fuel were reviewed in consideration of the particular time and temperature conditions. After careful consideration, the use of a 60^{o}C conditioning temperature for a 2500-hour exposure was identified as applicable for the defined purpose of evaluating response of the dispensing equipment.

Based on input from manufacturers, 60^{o}C corresponds well to a peak operating ambient for the equipment; while the equipment will not be continuously exposed to that temperature in use, testing at that temperature provides some useful practical information. Elevation of the conditioning temperature above 60^{o}C could theoretically permit reduced test time; however, exposure of the equipment to such temperatures would present practical challenges in performing the tests and may possibly have a negative effect on the rate of chemical reaction. Reduction of the test temperature would also be feasible, but would require extended testing time. For these reasons, 60^{o}C was selected as the most appropriate equipment conditioning temperature.

Gasket and seal materials are typically exposed to test fluids for 70-hour periods prior to assessment on the material level. In addition to the equipment exposure protocols outlined above, test exposure times longer than the typical 70-hour exposure were reviewed by test as a part of the gasket and seal material test program.

Gasket and Seal Research

The objective of the research on gasket and seal materials was to validate information that had not been supported with specific test data, and assess the effects of a number of important variables on material compatibility assessments.

Gasket and Seal Test Procedures
The program consisted of subjecting a number of gasket and seal materials to a variety of test conditions. Assorted samples of four seal materials were exposed to:

- Test fluids comprised of 25% and 85% ethanol;
- Test fluids with and without aggressive components;
- Exposure times of 70h, 140h, 210h, and 1000h;
- Room temperature exposure at 23^{o}C and 60^{o}C exposure;
- Both the test fluids and water at 60^{o}C, in order to assess the effects of temperature alone versus actual chemical attack; and
- Test fluids with corrosion inhibitor added in prescribed amounts, to assess possible effects of optional corrosion inhibitors on seal materials.

At the conclusion of the appropriate exposures, specified samples were subjected to tensile strength and elongation, volume change, weight extraction, and compression set assessments based on requirements in the Standard for Gaskets and Seals, UL 157.

Gasket and Seal Test Results
Many of the samples yielded results that would be compliant with the requirements of UL 157. However, noncompliant results were also observed. Because seals play a critical role in preventing loss of fuel containment, these findings underscore the need for proper definition of seal compatibility testing requirements in order to permit proper selection of gasket and seal materials for use in application where exposed to high-percentage ethanol fuel blends.

Information shared with UL, and available literature, had indicated for most materials, the 25% ethanol test fluids would tend to have more potentially degrading effects on seal materials. The data generated from the tensile strength, elongation, volume change, and extraction tests supports this premise. However, while almost all data from the exposure to the 25% ethanol test fluid indicated more degradation than exposure to the 85% ethanol test fluid, data also indicated the 85% ethanol test fluid may cause more degradation for some materials. For this reason, tests with both 25% and 85% ethanol test fluids have been required.

Overall, data for samples exposed to aggressive and non-aggressive fluids showed some level of correlation between test fluid and product performance, especially for volume change, extraction, and compression set. However, the data indicated that in some cases significantly more degradation may occur from the aggressive fluid than the non-aggressive fluid. For this reason, to best model practical usage with contaminated fuels, and to promote consistent test methodologies, testing with the aggressive fluids has been required.

Samples exposed to the test fluids for longer than 70h tended to demonstrate more degradation than those exposed for 70h. Similarly, samples exposed to elevated temperature fluids demonstrated more degradation than corresponding samples exposed to the same fluids for the same time at room temperature. Elevation of the test temperature, based on the Arrhenius principle, will correspond to increased chemical interaction. Samples exposed to water at 60^{o}C performed significantly better than samples exposed to ethanol test fluids at 60^{o}C, demonstrating that the reduction in performance for samples exposed to test fluids at 60^{o}C may be attributed to chemical attack and not only material property changes due to elevated temperature. Data generated from 70h exposures at 60^{o}C generally correlated to data from 1000h exposures at 23^{o}C. Based on this, testing either for 70h at 60^{o}C, or for 1000h at 23^{o}C may be appropriate. However, testing at room temperature provides major practical benefits. Additionally, the formed gaskets are also subjected to the 2500h/60^{o}C exposure conditions as part of the equipment assessment. For these reasons, gasket and seal material tests after exposure for 1000h at 23^{o}C have been required.

Data from samples exposed to test fluids incorporating corrosion inhibitor demonstrated little to no effect on seals.

Gasket and Seal Requirements

Requirements for the gasket and seal materials used in E85 dispensers were based on these findings and published in August 2007. The requirements specify exposure of gasket and seal materials for 1000h to both CE25a and CE85a test fluids at 23^{o}C. For static seals (seals not subject to movement in application), volume change, extraction, and compression set tests are required. For dynamic seals (seals subject to movement in application), tensile strength, elongation, volume change, and extraction are required. Seals intended for static/dynamic applications would need to comply with all applicable tests. Tensile strength and elongation after exposures may not be less than 60% of the as-received values. Volume change after exposure may not result in more than 40% increase or more than a 1% decrease. Extraction may not result in more than a 10% weight loss after exposure. Based on established best practices, compression set is required to be 35% maximum.

In addition to these material-level performance requirements for gasket and seal materials, samples of the formed gaskets and seals will also be tested within the equipment during the 2500h/60^{o}C equipment exposure tests for their ability to prevent leaks.

2500h Conditioning Exposure

The objective of the 2500h conditioning of the dispensing equipment was to review the effects of ethanol test fluids, time and temperature conditions as they relate to material compatibility assessments.

2500h Conditioning Exposure Test Procedures

This portion of the research program consisted of exposing nearly 40 samples of dispensers and dispenser components to test fluids at elevated temperature.

Two samples of each assembly were tested, with one exposed to CE25a and the second exposed to CE85a. The samples were conditioned for a total of 2500 hours at an elevated temperature of 60^{o}C. The test fluids were removed and replenished on a weekly basis to promote continued chemical interaction of the fluids with the test samples. During the weekly drain/refill process, the chamber permitted to cool; chamber cool-down and warm-up times were not included in the 2500h total. Test fluids drained from the samples were retained for analysis. During the weekly drain/refill sessions, the dispenser samples were also subjected to a 75 psi leakage test, representing 150% of a nominal dispensing system pressure of 50 psi.

2500h Conditioning Exposure Test Results

The majority of the samples did not demonstrate any leakage during the course of the 2500h exposure. However, one sample that had been exposed to CE25a exhibited leakage and damage to the seal. After completing approximately 75% of the exposure time, the sample did not comply with the weekly 75 psi leakage test. The sample was removed from the test chamber at that time.

Visual examination of the extracted test fluids each week showed discoloration compared to virgin test fluid, and indicated that the test fluids had acted upon the test samples. The extent of action, and any corresponding effect on safe performance of the equipment, was judged by the safety performance-testing regimen that followed the conditioning exposure.

Safety Performance Testing

The samples of dispensing equipment exposed to the conditioning exposure program were subjected to the safety performance tests contained in applicable UL Standards. The objective of this activity was to assess the performance of safety related functions of the dispenser products after exposure to high percentage ethanol test fluids.

Safety Performance Test Procedures

Samples of each product design that successfully completed the conditioning exposure were then subjected to critical performance tests from the applicable UL standards covering the devices for petroleum service.

Hose nozzle valves were subjected to tests from the Standard for Valves for Flammable Fluids, UL 842. Tests included:

- External Leakage Test (Section 13), consisting of 75 psi pressure testing with valve closed/outlet open, and 25 psi pressure testing with valve open/outlet closed;
- Endurance Test (Section 21) to assess the ability of the valve to operate and stop the flow of fluid for 100,000 cycles;
- External Leakage Test repeated after the Endurance Test;
- Hydrostatic Strength Test (Section 22) at 250 psi; and

- Electrical Continuity Test (Section 23), to assess the ability of the product to maintain electrical continuity.

Breakaway couplings were subjected to tests from the Standard for Emergency Breakaway Fittings, Swivel Connectors, and Pipe-Connection Fittings for Petroleum Products and LP-Gas, UL 567. Tests included:

- Electrical Continuity Test (Section 12), to assess the ability of the product to maintain electrical continuity under no pressure and rated pressure conditions;
- External Leakage Test (Section 13), consisting of 75 psi pressure testing;
- Pull Test (Section 20.2), to ensure that the breakaway separates at an appropriate value based on its rating; and
- Seat Leakage Test (Section 14), to assess adequate closure of the breakaway sections after separation.

Valves actuated by electrical means were subjected to tests from the Standard for Electrically Operated Valves, UL 429. Tests included:

- External Leakage Test (Section 28), consisting of 75 psi pressure testing;
- Seat Leakage Test (Section 29), to assess adequate closure of the valve;
- Endurance Test (Section 30) to assess the ability of the valve to operate and stop the flow of fluid for 100,000 cycles; and
- External Leakage Test and Seat Leakage Test repeated after the Endurance Test.

Meters were subjected to tests from the Standard for Meters for Flammable and Combustible Liquids and LP-Gas, UL 25. Tests included:

- Leakage Test (Section 12), consisting of 75 psi pressure testing;
- Endurance Test (Section 13) to assess the ability of the meter to withstand 300 hours of flow without leakage through the shaft or other locations; and
- Leakage Test repeated after the Endurance Test.

Safety Performance Test Results

The results from the performance-testing program are summarized in Table 1. The intent of the test regimen was to have a sample of each product design exposed to each test fluid, and subsequently subjected to the appropriate performance tests from the relevant standard. In some cases, multiple samples of the same product design were exposed to the test fluids. Each conditioned sample was subjected to an External Leakage Test at the conclusion of the exposure. However, each conditioned sample of every product design was not subjected to the full range of performance tests. In the interest of clarity, only test results for samples subjected to the full range of appropriate performance tests are shown.

Table 1 – Summary Of Performance Testing Program Findings

Part	Test Fluid	Tests [a]	Results & Comments
Hose Nozzle Valve Design #1	CE85a	EL, E, ELR, H, EC	External Leakage, Endurance, Hydrostatic & Electrical Continuity Test results were compliant. During External Leakage Test repeated after Endurance, leakage occurred through the vacuum cap with the valve open/outlet closed. Noncompliant.
Hose Nozzle Valve Design #2	CE25a	EL, H, EC, E	Component level sample. External Leakage, Hydrostatic, and Electrical Continuity Test results were compliant. Sample would not open and could not be shown to pass the Endurance Test.
Hose Nozzle Valve Design #2	CE25a	EL, E, H, ELR, EC	System level sample. All results compliant.
Hose Nozzle Valve Design #2	CE85a	EL, H, EC, E	Component level sample. External Leakage, Hydrostatic, and Electrical Continuity Test results were compliant. Sample would not open and could not be shown to pass the Endurance Test.
Hose Nozzle Valve Design #2	CE85a	EL, H, C	System level sample. External Leakage, Hydrostatic, and Electrical Continuity Test results were compliant. Sample would not open and could not be shown to pass the Endurance Test.
Hose Nozzle Valve Design #2	CE85a	EL, E, H ELR, EC	System level sample. All test results compliant.
Breakaway Coupling	CE25a	EC, EL, SL, P	All test results compliant.
Breakaway Coupling	CE85a	EC, EL, SL, P	All test results compliant.
Valve Design #1	CE25a	EL, SL	No leakage at the conclusion of the 2500-hour exposure. Sample showed leakage at approximately 11,000 cycles during the Endurance Test. Noncompliant.
Valve Design #1	CE85a	EL, SL, E, ELR, SLR	All test results compliant.
Valve Design #2	CE25a	EL, SL, E	All test results compliant.
Valve Design #2	CE85a	EL, SL, E	All test results compliant.
Valve Design #3	CE25a	EL, SL, E	All test results compliant.
Valve Design #3	CE85a	EL, SL, E	All test results compliant.
Meter Design #1	CE25a	EL, E, ELR	No leakage at the conclusion of the 2500-hour exposure. The sample was unable to complete the Endurance Test and stopped flow after approximately 83% completion. When Leakage Test was repeated after the Endurance Test, leakage occurred.
Meter Design #1	CE85a	EL, E, ELR	No leakage at the conclusion of the 2500h exposure. When Leakage Test was repeated after the Endurance Test, leakage occurred. Noncompliant.
Meter Design #2	CE25a	None	Sample not tested due to leakage during the 2500h exposure.
Meter Design #2	CE85a	EL, E	No leakage at the conclusion of the 2500h exposure. During the Endurance Test, after approximately 8% completion, leakage occurred. Noncompliant.
Meter Design #3	CE25a	EL, E	Leakage occurred after Endurance.
Meter Design #3	CE85a	EL, E	Leakage occurred after Endurance.

Table 1 Note:
a - Test codes designate the following tests, performed as required by the applicable UL standard:

E	Endurance test
EC	Electrical Continuity
EL	External Leakage at 75 psi
ELR	External Leakage, repeated after Endurance Test
H	Hydrostatic test at 250 psi
P	Breakaway pull test
SL	Seat Leakage at 75 psi
SLR	Seat Leakage, repeated after Endurance Test

While the performance of some test samples was good, the overall test results support the conclusion that high percentage ethanol fuels can degrade materials. This material degradation can in turn affect the ability of the products to meet the safety performance requirements contained in UL's standards. This was manifested in the sample population in the form of leakage from sealed joints on the equipment, gumming of seals, locking of moving parts in a manner that prohibits non-safety related functionality, and some visual evidence of corrosion.

The majority of the noncompliant test results were generated by the root cause of gasket or seal failure. Improved selection of gasket and seal materials should provide a significant improvement in the ability of designs to comply with test requirements. Sectioning analysis of the test samples showed some corrosion in the fuel path, although test results indicated that most action on the metallic structures did not result in degradation that could lead to a safety concern. The exception would be the mechanisms causing the hose nozzle valves and meters to become inoperable; while the test samples did not demonstrate leakage, the locking of internal moving parts is undesirable.

As previously noted in the gasket and seal research program, testing with CE25a fluids can be more degrading in some cases than testing with CE85a. This pattern was noted in the performance testing as well. Several products showed better performance for samples exposed to CE85a than samples exposed to CE25a.

The issue of galvanic interaction at metallic interfaces is one that is important to address for high percentage ethanol/gasoline fuel blends. Galvanic interaction may be addressed by requiring all testing on a system level (i.e. testing every permutation of all component interfaces through the fuel path); however, there are significant practical benefits to being able to test subassemblies discretely and specify permitted combinations for connection in the factory or field. Some of the discrete component samples were identical to those built into the dispenser samples, but the discrete samples were capped off with plugs made of the same material that they were to be connected to in the dispensers. The relative performance of the discrete samples supported component level testing to address galvanic interaction. The 2500h exposure test is to be conducted on a component level with plugs of the most galvanically incompatible materials permitted by the manufacturer. At this time, in the absence of information specific to high percentage ethanol/gasoline fuel blends, the "Galvanic Series of Metals Exposed to Seawater" Table from the *NACE Corrosion Engineer's Reference Book,* published by NACE International, has been identified as the most appropriate basis for the determination of galvanic incompatibility. Materials permitted by the manufacturer but not included in this Table are addressed by subjecting samples employing the material interface to the 2500h test.

Many gasket and seal materials swell when exposed to ethanol. When exposure is ended, the seals may exhibit a reduction in volume known as "dry-out." After exposure to the ethanol fluids was terminated in the research, the tendency of the gaskets and seals to dry out rapidly was noted in the handling of the test samples. The practical effect on the research testing was minimal. However, this phenomenon underscored the need to include measures in the requirements to minimize the risk of leakages in practice due to dry-out.

Analytical Testing

Analytical tests were performed on the ethanol-blended test fluids that were drained from samples of dispensers and dispenser subassemblies used in the 2500h conditioning exposure. The objective of this activity was to analyze the extracted test fluids in order to identify various extracted or deposited elements and organic compounds resulting from the exposure of the equipment to the high percentage ethanol test fluids. The analytical procedures focused on both inorganic and organic compounds.

Analytical Test Procedures

Two types of analytical procedures were used to analyze the test fluids. Inductively Coupled Plasma/Mass Spectroscopy (ICP/MS) was used to analyze an aqueous extract of the test fluids. Gas Chromatography/Mass Spectroscopy (GC/MS) was used to analyze the entire test fluid sample (including water, acids and salts).

The samples for ICP/MS analysis were prepared by first adding a combination of a 5% acid solution and a water-insoluble organic solvent to the test fluid samples. This mixture was then shaken to achieve an even distribution of the fluids. After the sample was allowed to rest, two distinct layers were formed:

a) An organic layer, which contained the water-insoluble organic content of the fluids, and
b) An aqueous layer that was assumed to contain any water-soluble inorganic elements arising from metallic corrosion of the equipment samples.

The ICP/MS analysis was specifically focused on nineteen separate elements: aluminum, antimony, barium, beryllium, cadmium, chromium, copper, iron, lead, lithium, manganese, molybdenum, nickel, silver, thallium, tin, titanium, vanadium, and zinc.

The GC/MS organics analysis consisted of testing the unmodified fluid samples (fluid directly from the samples including water, salts and acids) against references. These included a reference standard library of 40 compounds as well as the use of Wiley Library's search library of approximately 200,000 compounds for the identification of TICs (Tentatively Identified Compounds) based upon the retention times of internally added reference compounds.

Analytical Test Results

The ICP/MS and GC/MS data indicated that CE25a and CE85a test fluids exhibit different behavior against the metals and polymeric materials of the dispenser components. Differences in the both concentration and ranking of inorganic elements arising from the samples were noted, with those in extracted CE85a being more pronounced. The organics analysis shows less of a differential effect between the two fluids. These results reinforce the need to use both the CE85a and CE25a test fluids.

The ICP/MS analysis indicated the presence of high concentrations of zinc and aluminum in the aqueous phase for both CE25a and CE85a fluids. Lesser concentrations of copper, nickel, tin, iron, lead and barium were measured in both types of extracted test fluids. Additionally, comparisons between element compositions in the test fluids drawn from plated and unplated samples show that the use of plating (typically nickel) and surface treatments (such as anodizing) is generally effective as a means to mitigate the extraction of material.

Substantial extraction of organic compounds was noted for CE25a and CE85a test fluids. Over 200 organic compounds were extracted from the assorted equipment under test. The extraordinary number of extracted compounds includes significant levels of plasticizers, stabilizers, polymer modifiers, oligomers, and antioxidants. The effects of the removal of these compounds is evident in the resultant performance of the formed parts in the safety performance testing program, especially as it relates to the performance of seals.

The presence of significant numbers and levels of extracted material in the test fluids may indicate a potential effect on fuel quality. The research test protocol that was used exposed the equipment to the test fluid for a one-week period at elevated temperature to accelerate the chemical interaction of the fluid with the equipment. Accordingly, the concentrations of extracted compounds in the test fluid would be expected to be higher than concentrations in practical dispensing of ethanol fuel. However, the tendency of the ethanol fluids to extract both organic and inorganic materials over time from the dispenser path was noted. The issue of fuel quality is independent of the safety certification of the dispenser equipment, and was not within the scope of this research program.

Harvested Sample Assessments

Samples of products from the field that had been in service dispensing high-percentage ethanol fuel blends were harvested. These harvested samples were analyzed, and when possible, subjected to performance testing from the UL Standard that would cover the device for petroleum service. The objective of this activity was to obtain information from examinations and assessments of products that have been in actual service with high percentage ethanol fuel blends.

In February 2007, UL published "*Survey of E85 Dispensing Operations in the U.S.*" documenting findings from visits to E85 dispensing locations in the United States. In March 2007, "*Ethanol Fuel Dispensing Operations in Brazil*" was published. The results of these qualitative surveys indicated a favorable history of dispensing high percentage ethanol fuel blends, but based on practical limitations did not allow for the generation of test data.

Numerous samples of components and dispensers were harvested from a variety of sources. Many of the products had been in service dispensing hydrated ethanol fuel (without the gasoline component) in Brazil; however, some of the samples had been in use in the United States. The usage conditions for the harvested samples range from short-time use to multi-year use, dispensing a variety of fuels. For some samples, specific use conditions were not available. Samples were obtained from equipment manufacturers and independent users.

Harvested Sample Test Procedures

The samples were subjected to leakage testing and relevant safety performance testing from the applicable UL standard covering the type of equipment for petroleum service, as previously noted. The applicable tests from the UL standards are “type tests” - meaning that dedicated test samples are subjected to the test protocol rather than samples that have been in actual service. However, in assessing the ability of these harvested samples to contain fuels and to perform their intended safety functions, the applicable UL type tests were identified as the best analytical method. Further, the general approach of performance testing after fuel exposure follows the conceptual plan of the conditioning research.

Harvested Sample Results

The harvested samples demonstrated degradation across a continuum that may correspond to wide conditions of use, length of use, and conditions of maintenance. Some of the samples showed no signs of degradation and were in premium condition. Some samples showed degradation and did not comply with applicable tests. The compliance of other samples could not be verified because of their condition. The results from the harvested sample test program are summarized in Table 2.

Table 2 – Summary Of Harvested Sample Findings

Part	Fuel Dispensed	Service (Yrs)	Volume (Gal)	Tests [b]	Comments
Dispenser	E85	Unknown	Unknown	L	No leakage.
Dispenser	E85	7	Unknown	L	No leakage
Filter casting/ filter element	Hydrated ethanol[a]	7	Unknown	L, V	No leakage. No visible deterioration. [e]
Filter casting/ filter element	Hydrated ethanol[a]	2	29,059	L, V	No leakage. No visible deterioration. [e]
Hose breakaway	Hydrated ethanol[a]	2.5	39,626	P	Separated at 400 lbs; inconclusive. [c]
Hose	E85	7	Unknown	L	Results compliant.
Hose	E85	7	Unknown	L	Leakage at coupling at 8 psi.
Hose breakaway	E85	7	Unknown	EC, L, P	Seat leakage after Pull test noncompliant.
Hose breakaway	E85	7	Unknown	EC, L, P	Separated at 593 lbs.; noncompliant. Seat leakage after Pull test noncompliant.
Hose nozzle	Hydrated ethanol[a]	1	5812	A, L, V	No leakage. Analytical tests on white residue.
Hose nozzle	Hydrated ethanol[a]	2	7793	L,V	No leakage. Traces of white residue.
Hose nozzle	Hydrated ethanol[a]	3	9775	L,V	No leakage. Traces of white residue.
Hose nozzle	Hydrated ethanol[a]	3.5	10,270	A, L, V	Leakage from spout at 20 psi. Analytical tests on white residue.
Hose nozzle	Hydrated ethanol[a]	7	Unknown	H, L	Results compliant.
Hose nozzle	Hydrated ethanol[a]	7	Unknown	H, L	Results compliant.
Hose Nozzle	E85	7	Unknown	EC, L	Results compliant.
Hose Nozzle	E85	7	Unknown	EC, L	Results compliant.
Hose nozzle /hose/breakaway	Hydrated ethanol[a]	2.5	39,626	H, L	Hydrostatic passed. No leakage.
Meter	E85	3	13,000	L, V	Results compliant.
Meter	Hydrated ethanol[a]	7	Unknown	L, V	Sample showed noncompliant leakage test results at 7 psi. No visible deterioration. [d]
Meter body / manifold casting	Hydrated ethanol[a]	2.5	39,626	V	Sample not complete and could not be tested. No visible deterioration.
Meter	E85	7	Unknown	L	Results compliant.
Hose nozzle /hose/breakaway	E85	Unknown	Unknown	L, P	Results compliant.
Nozzle breakaway	Unknown	Unknown	Unknown	L	Leakage at 20 psi.
Nozzle breakaway	Unknown	Unknown	Unknown	V	Sample broke while attaching pipe for leakage test. Signs of wear.
Nozzle breakaway	Unknown	Unknown	Unknown	L	Results compliant.
Pressure actuator assembly	E85	Unknown	Unknown	L	Leakage at 25 psi.
Swivel	Unknown	Unknown	Unknown	L	Results compliant.
Swivel	Unknown	Unknown	Unknown	L	Results compliant.
Swivel	Unknown	Unknown	Unknown	L	Results compliant.
Swivel	Unknown	Unknown	Unknown	L	Results compliant.
Swivel	E85	7	Unknown	EC, L	Results compliant.
Swivel	E85	7	Unknown	EC, L	Results compliant.
Solenoid valve	E85	3	13,000	L, V	Results compliant.
Solenoid valve	Hydrated ethanol[a]	Unknown	Unknown	V	Sample incomplete and could not be tested. No visible deterioration.
Solenoid valve	Hydrated ethanol[a]	2.5	39,626	V	Sample not complete and could not be tested. No visible deterioration.

Table 2 Notes:
a - Brazilian hydrated ethanol fuel, nominally 93% ethanol / 7% water.

b - Test codes designate the following testing and analytical procedures:

A	Analytical analysis of residues
E	Endurance test
EC	Electrical Continuity test
H	250 psi hydrostatic test
L	75 psi leakage test
P	Breakaway pull test
V	Visual examination

c- Breakaways are required to separate at a force that is above 100 lbs and not more than their rated value, which is marked on the breakaway. Due to wear and build-up of residue it was impossible to determine the marked separation rating to verify compliance with the rated value.

d - The harvested sample was incomplete and needed to be mated with other parts in order to be tested. The sample has three connection points and four additional closures. New mating parts and o-rings were connected to the three connection points of the harvested sample to complete the leakage test. Leakage was observed through the four unmodified closures. The modified connection points complied with the leakage test requirements.

e - The harvested samples were incomplete and needed to be mated with other parts in order to be tested. New mating parts and gaskets were connected to the harvested samples to complete the leakage test. The resultant assemblies complied with the requirements after these modifications.

Practical considerations limit the conclusions that can be drawn from testing of harvested samples, some of which have unspecified usage history and have been removed from service for undefined reasons and periods. However, acknowledging these limitations, the harvested sample research program provided useful information.

While many harvested samples in this limited population performed well, the noncompliant results indicate that high percentage ethanol fuel blends can degrade materials and possibly result in degradation to products that may affect their ability to meet the performance requirements of UL's standards. This was manifested in the harvested sample population primarily in the form of leakage from sealed joints on the equipment. Visual evidence of degradation was also noted in some cases.

Several samples demonstrated deposits of white residue in the form of deposited powder on the interior surfaces of the fluid path. This powder was removed and subjected to chemical analysis in order to determine the constituents of the residue. The analysis indicated the presence of chromium, copper, iron, magnesium, manganese, and zinc. The results did not demonstrate the presence of aluminum, which formed the major material used in the construction of this equipment. It appears that the residue was result of contaminated fuel being handled by the equipment, although information on the source of the residue is not conclusive.

Equipment Requirements

After reviewing the equipment research test results, the equipment testing protocols were defined. Samples are required to be exposed to CE25a and CE85a test fluids for a period of 2500h at 60^{o}C. The samples are prepared with plugs of the most galvanically incompatible materials, and as needed other materials of undefined galvanic incompatibility. At the conclusion of the 2500h exposure, the samples are subjected to the applicable safety performance tests from applicable UL standards.

The evaluation strategy using both CE85a and CE25a test fluids yields many benefits. This strategy best addresses the reactions of both metallic and non-metallic dispenser materials in the concentrations most likely to cause degradation. Testing with both fluids addresses the present range of E85 fuel blends based on seasonal and geographical variations. This strategy also accommodates blending dispenser designs that may have variable ethanol percentages in the fuel path. The strategy also anticipates ethanol/gasoline fuel blends in the 15^{+} to 25% ethanol range that are not yet nationally available, but are being piloted in Minnesota and under strong consideration for future usage on a national scale with all vehicles accepting gasoline. Finally, the plan presents a single, clear rating for products intended for ethanol blended fuel use that will simplify acceptance by Authorities Having Jurisdiction and other interested parties.

The research demonstrated that the action of the CE25a fluid and the consequential effects on materials are different than that of the CE85a fluid. The research has also shown that commercially available dispenser products can be designed to meet requirements. In some cases more careful selection of gasket and seal materials in particular may be needed to address the lower ethanol concentration represented by the CE25a test condition.

The defined research program met its objective of permitting the identification of requirements for the design and performance of dispensing equipment for high percentage ethanol/gasoline fuel blends. These detailed requirements are documented in the Outline of Investigation for Power-Operated Dispensing Devices for Gasoline/Ethanol Blends With Ethanol Content Greater than 15%, Subject 87A, which was published by UL in October 2007. A second edition was published in November 2007 with additional requirements for vapor recovery. The requirements define performance-based protocols for assessment of the safety of a variety of materials integrated into a particular dispensing equipment design.

Conclusion

The research program has validated important premises and has supported the development of a test regimen and certification program for E85 dispensers.

The data generated during the program shows that some commercially available materials and equipment would be expected to comply with the certification requirements and be suitable for use with E85. Additionally, some of the harvested products in use dispensing high percentage ethanol/gasoline fuel blends were in good to excellent condition. These results indicate that proper material selection, material application, and equipment design can be practically implemented to accomplish safe dispensing of E85.

Some commercially available materials or equipment may not pass the necessary requirements, or may not pass the necessary requirements for a particular application. The test data clearly demonstrate high percentage ethanol/gasoline fuel blends can act in a significant manner on materials in the fuel path of a dispenser, can degrade materials that are not appropriately selected or applied, and can negatively affect the safe performance of the equipment. Careful selection and application of appropriate materials for use in E85 dispensers is necessary. In particular, careful selection and application of seal materials is expected to produce a significant and rapid improvement in the performance of these products.

UL has established appropriate equipment testing methodologies and certification requirements for dispensing equipment intended for use with high percentage ethanol/gasoline fuel blends. The requirements constitute reasonable measures to mitigate the effects of exposure to these fuels.

While the immediate goal of defining requirements for the safety of dispensing equipment has been addressed, there are ongoing efforts to build additional technical insight into the effects of dispensing high percentage ethanol/gasoline fuel blends on materials and equipment. The US Department of Energy (DOE) is leading work to which UL and others are providing knowledge support related to research of fire characteristics of E85 blends. UL is collaborating with DOE, Oak Ridge National Laboratories, the National Renewable Energy Laboratory, and the Environmental Protection Agency's National Vehicle Fuel Emissions Laboratory to conduct additional experiments with moving test fluids. Other research work may be appropriate to address this quickly developing sector. Organizations having responsibility for fuel quality and collateral effects of extracted compounds in high percentage ethanol/gasoline fuel blends for internal combustion engines may need to consider future research.

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