Assessment of the Effectiveness of Three Aftermarket Gasoline Fuel Stabilizers in Preventing Gum Formation and Loss of Oxidation Stability

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Abstract

Fuel stabilizers have long been marketed to consumers to prevent oxidation and gum formation. In the past, gasoline storage for long periods of time was commonly limited to off-road equipment that was used infrequently. Cars and trucks that were driven regularly consumed the fuel in their tanks rapidly enough to avoid excessive fuel aging. However, plug-in hybrid electric vehicles (PHEVs) may be operated frequently without engine operation, raising the possibility that fuel may be stored in the tank for longer periods of time. There is little if any scientifically backed information available to consumers to aid them in assessing the need to use an aftermarket fuel stabilizer if they anticipate lengthy periods of fuel storage in their fuel tank. This study was conceived to address this information gap by evaluating three aftermarket stabilizer products alongside baseline gasoline using sealed samples over a period of 12 months of aging. The aging was carried out under ambient temperature conditions with an additional series of samples kept in refrigerated storage. Analyses of vapor pressure, copper strip corrosion, oxidation stability, existent gums, and potential gums were carried out using standard ASTM tests to evaluate the samples as aging progressed. The results show that baseline gasoline remained compliant with relevant specifications to at least 12 months of aging without the use of aftermarket stabilizer additives. Use of two of the aftermarket additives increased the oxidation stability of the baseline gasoline, but this added stability was not necessary to comply with gasoline specifications.

Introduction

Fuel stabilizers have long been marketed to small engine owners as a means of avoiding equipment malfunctions caused by aged gasoline. Gasoline that is stored for extended periods can experience auto-oxidation to form gums and varnishes that can cause deposits when introduced into the fuel system. This problem has historically been limited to off-road equipment, where fuel may remain stored for extended periods. Automobiles that are driven regularly have not been at risk because the fuel in the tank is consumed over a relatively short period of time. However, PHEVs may be driven regularly as an electric vehicle (EV) without regular engine operation. In this case, the engine may not be used enough to consume the fuel in the tank before it undergoes oxidation to form gums.

ASTM standard D4814 specifies the properties for gasoline sold in the U.S. [1] Manufacturers commonly use additives (such as antioxidants) to assure that the gasoline sold at the pump meets or exceeds the specifications in D4814 and applicable federal law. [2] The standard includes specifications for corrosivity to copper strips, existent gums, and oxidation stability. These three properties are useful in examining potential degradation of gasoline caused by aging.

The specific chemical formulation of gasoline additives, whether used in gasoline manufacturing or those used in aftermarket additives, are considered by their manufacturers to be trade secrets. Additives can include antioxidant functionality to prevent the formation of gums and varnishes. They can also include detergents and dispersants that act to prevent and remove deposits. [2]

There are few, if any, scientifically backed studies available to the public that document the efficacy of any off-the-shelf fuel stabilizers. This information gap leaves consumers vulnerable to unfounded information that may cause them to use products they do not need or products that may do harm to their vehicles. This study aims to provide scientifically backed information to aid consumers in deciding whether they should consider using a fuel stabilizer.

Sample Preparation

Three additives were selected for inclusion in this study. All were obtained off-the-shelf from a retailer. These additives included Lucas Oil Products, Inc. Safeguard Ethanol Fuel Conditioner with Stabilizers, Sta-Bil 360° Protection Ethanol Treatment and Stabilizer, and Starbrite Star-Tron Enzyme Fuel Treatment. All three additives advertised fuel stabilization functionality on the label. The additive volumes in the retail containers were sufficient to treat larger volumes of gasoline than were needed to support this study. Smaller volumes of each additive were therefore measured and dispensed into glass vials in advance of gasoline acquisition for use with 5-gallon containers of gasoline. The appropriate volume of each additive to be used was calculated based on the maximum amount of gasoline that the additive package indicated could be treated. In this way, the minimum effective amount of additive could be added to 5-gallon containers of gasoline.

Gasoline was obtained at the pump from a major regional retailer that is not listed as a supplier of top tier fuel. A 5-gallon container of gasoline was assigned for each additive and prepared by first pumping approximately 1 gallon of gasoline into the container. The pre-measured volume of additive was then poured into the gasoline, and the remainder of the 5 gallons of gasoline pumped into the container. This process was repeated for each additive. Five-gallon containers of gasoline were also prepared for baseline samples that were not additized. Finally, a 5-gallon container of gasoline was procured from a different major retailer that was listed as a supplier of top-tier fuel for use as another comparative sample in the study. All batches of gasoline were regular-grade (87 antiknock index) and contained nominally 10% ethanol. Acquisition of all batches of gasoline took place the same day.

Three-liter samples were then created using the 5-gallon batches of gasoline. Each sample was contained in a 3.785 liter (1 gallon) epoxy-lined steel can. The remaining headspace was approximately 0.785 liters, or 20% of the can volume. The cans were filled outdoors so that the headspace contained humid ambient air. Once filled, each sample can was sealed. Sample cans were created for aging times of 0, 1, 2, 3, 6, and 12 months for each additive blend and the baseline and top tier gasoline samples. Samples for the three additives were denoted using the letters A, B, and C. The top tier samples were denoted with the letter D. Two sets of baseline gasoline samples were created, denoted with the letters E and F. Sample sets A – E were placed in a covered outdoor space away from direct sunlight. Sample set F was place in a refrigerated storage building.

Results

Initial Samples at Study Inception

The 0 month aging samples (A0, B0, C0, D0, and E0) were sent for analysis at the inception of the study. Sample F0 was not sent for analysis as it was the same material contained in sample E0. All ASTM tests were conducted by Southwest Research Institute.

Samples D0 (Top Tier) and E0 (Baseline) were subjected to a detailed hydrocarbon analysis using the ASTM D6730 method. [3] Results of this test for both samples are shown in Figures 1 and 2. The chemical makeup of the two fuels is similar, despite the fuels being sourced from two different retailers. Of particular interest to this study is the olefin content because olefins are known to be susceptible to oxidation and gum formation. [2] For several reasons, olefin content is limited in gasoline. For example, the California Air Resources Board limits olefins to 10% in gasoline sold in California.

ASTM D381 measures the mass of gums present in a 100 ml sample of gasoline. [4] During the test the sample is evaporated under controlled conditions using a jet of air. The test measures both the unwashed and washed gums. Unwashed gums are the total gums remaining when the sample has evaporated. Unwashed gums include nonvolatile additives (such as detergents and antioxidants) in the sample as well as gums that have formed due to gasoline oxidation. Washed gums are the gums that remain after washing the gums with a solvent to remove gums that are soluble in gasoline. Washed gums

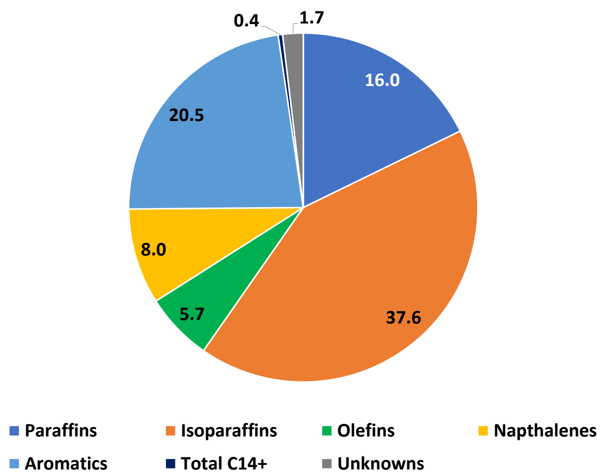

Figure 1. Volume % of each major chemical family present in the baseline gasoline sample (E0).

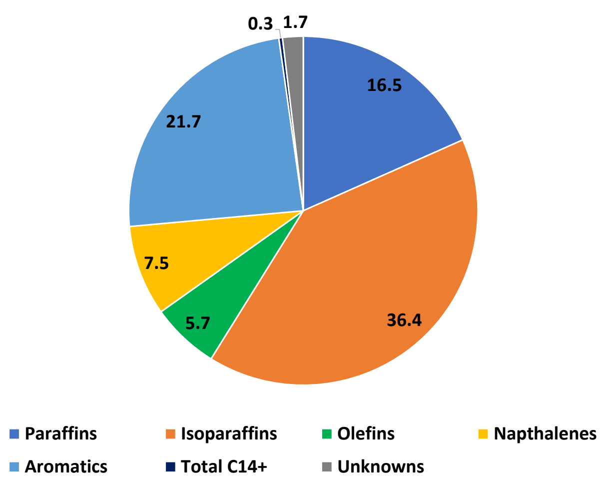

Figure 2. Volume % of each major chemical family present in the Top Tier gasoline sample (D0).

are not soluble in gasoline and are indicative of a risk of deposit formation in the fuel system. Figure 3 shows the unwashed gum content for the initial fuel samples. Samples blended with additives A and B result in increased washed gums compared to the baseline sample, E. This result is consistent with these samples having increased levels of non-volatile compounds added to aid in protecting gasoline from the effects of aging. Sample C0 had an unwashed gum level comparable to the baseline, indicating that there were similar amounts of non-volatile components between these samples. Top

Tier gasoline contains greater amounts of detergent additives than non-Top Tier fuel. The washed gum level for sample D0 is higher than that of E0, and this result is consistent with the expected higher detergent level. Samples E0 and F0 (not shown) are expected to be the same since they are the same gasoline and have not undergone additional aging. The washed gum results for all samples were less than 0.5 mg/100ml. This level is the lowest reportable result for washed gums in this test. The ASTM D4814 gasoline standard limits washed gums to less than 5 mg/100ml. The initial samples are all well below specification for washed gums, as expected.

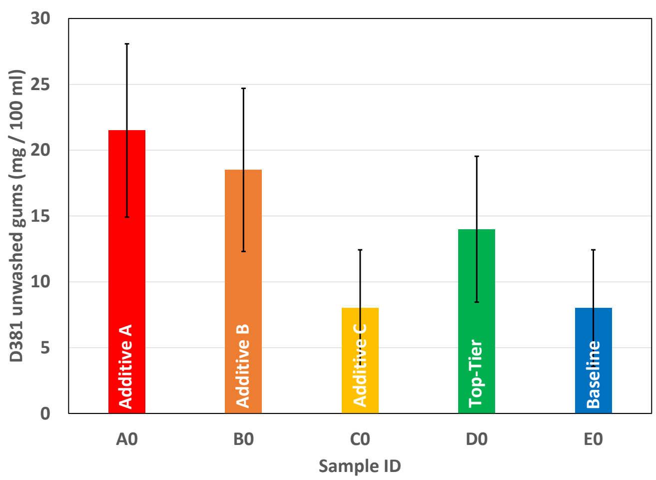

Figure 3. D381 unwashed gum results for the initial fuel samples. Error bars are the published reproducibility for D381.

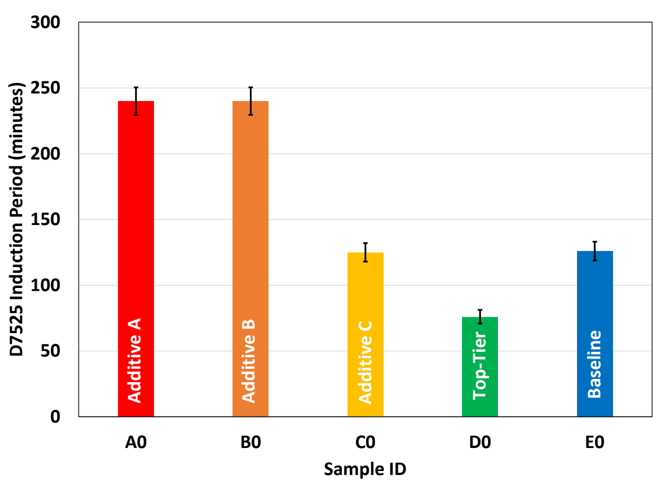

Figure 4. Oxidation stability of the initial fuel samples as measured by D7525 induction time. The error bars are the published reproducibility for the test.

ASTM D7525 is a rapid oxidation test to examine the oxidation stability of gasoline. [5] The sample is subjected to elevated temperature and pressure in the presence of pure oxygen to encourage rapid oxidation of the sample. This test was selected instead of the D525 test to seek differences among the fuel stabilizers. Results of the D7525 test are measured in minutes of oxygen induction time, with higher values being indicative of greater oxidation resistance. Results of this test for the initial fuel samples are shown in Figure 4.

Use of additive C did not raise the measured induction time significantly relative to the baseline gasoline sample. However, use of either additive A or B did raise the induction time significantly, indicating that both products contain effective antioxidant compounds. This result is consistent with the higher level of unwashed gums noted for these samples. The Top Tier sample yielded the lowest level of oxidation stability. Importantly, Top Tier specifications focus on increasing detergency (not oxidation stability) relative to non-Top Tier fuels. [6]

Aged Samples Through 12 Months of Aging

Sample aging was carried out for samples A, B, C, D, and E in a covered outdoor enclosure away from direct sunlight. The ambient temperature changed diurnally and seasonally. A temperature logger placed outdoors with the fuel samples recorded temperature every four hours; the temperature trend observed during the first 6 months of aging is shown in Figure 5. Unfortunately, a datalogger issue resulted in the loss of the temperature data from 6-12 months. However, the results from the first 6 months of aging likely capture the seasonal high and low temperatures of this trend. Temperatures at the beginning of the study exceeded 30°C during the day and dropped by about 10°C at night. As the study progressed the high and low temperatures noted each day dropped as fall and winter seasons occurred, with minimum temperatures below 0°C.

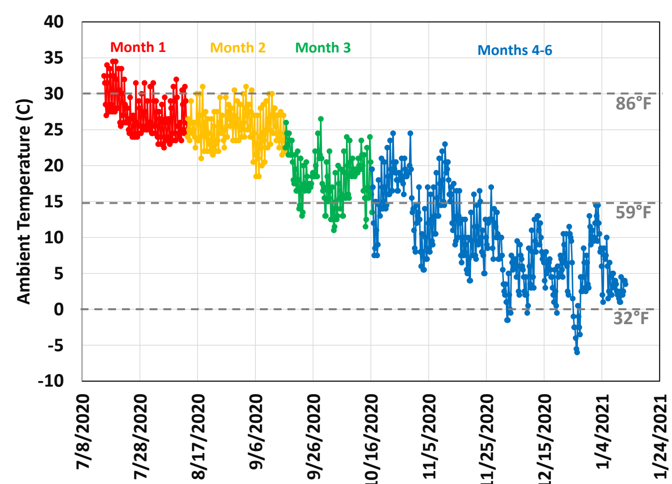

Figure 5. Ambient temperature data from the first six months of sample aging.

The F samples were kept in refrigerated storage to enable examination of the effect that storage temperature had on the progression of oxidation, if it occurred. The refrigerated storage facility was maintained at a near-constant temperature of 15°C, with typical excursions of ±2°C from the setpoint.

Dry vapor pressure equivalent (DVPE), a measure of the volatility of gasoline, was measured for all of the samples using ASTM D5191. [7] This measurement was conducted as a means of screening for samples that had experienced undesired evaporation during the aging period. Undesired evaporation of samples could occur if the bungs on the sample cans were not perfectly sealed at the beginning of the study. If evaporation occurred, it could skew the results from other measurements. Figure 6 shows the DVPE results for the study samples. The error bars shown are the published reproducibility for the test. Any sample experiencing evaporation should have a DVPE considerably lower than other samples. DVPE for all samples agreed within the published reproducibility of the test, indicating that there is no evidence that any samples experienced undesired evaporation during the aging period.

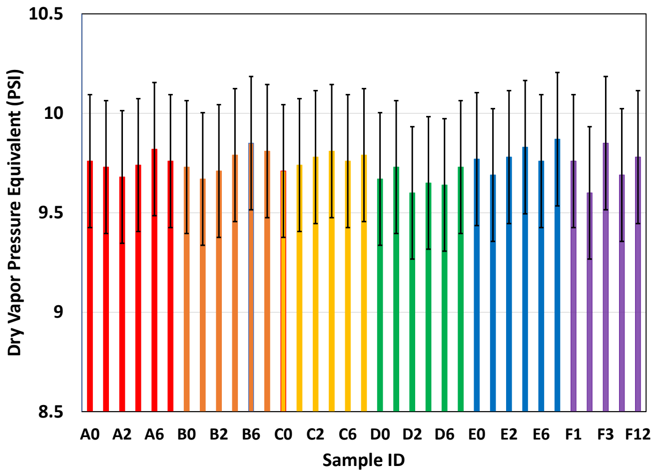

Figure 6. DVPE results for the study samples.

Copper Corrosion

The gasoline samples included up to 10% ethanol, raising the possibility that the ethanol could oxidize during aging to form acetic acid. Acetic acid is corrosive to metals. The D130 copper strip corrosion test was included in the study to assess this possibility. This test involves soaking a strip of polished copper in the sample for three hours. The vial containing the copper strip and sample gasoline is sealed and immersed in a water bath that keeps the sample at a constant temperature of 50°C. At the conclusion of the test, the sample strip is compared against a set of visual standards to assess the severity of corrosion. The results range from a best result of 1A showing only slight tarnish to 4C indicating corrosion. [8]

The D4814 gasoline specification requires that the result of the copper corrosion test be 1A. All samples in this study resulted in a 1A rating on the test. Based on these results, even the baseline gasoline remains compliant with copper corrosion specifications when aged for 12 months. Since 1A is the best result for the test, there is no opportunity for the aftermarket additives to improve this test result, and therefore they cannot provide an anti-corrosion benefit.

Gum Formation During Aging

The D381 test was again used for the aged samples to assess whether gums had formed during fuel aging. The unwashed gum results are shown for the D, E, and F samples in Figure 7. The error bars shown are the published reproducibility for the test. The D samples (Top Tier gasoline) exhibited the highest level of unwashed gums among these samples. This elevated level is consistent with these samples containing higher concentrations of detergent additives, for example, which is consistent with Top Tier gasoline requirements. The E and F samples are the same gasoline but they are aged at different temperatures. In all three cases (D, E, and F) the unwashed gum content of the samples remains consistent through the sample aging period of 12 months. Additionally, the washed gums content for these samples remained below 0.5 mg / 100 ml, well below the specified limit for gasoline. These findings indicate that none of these samples experienced gum formation during the 12 month aging period.

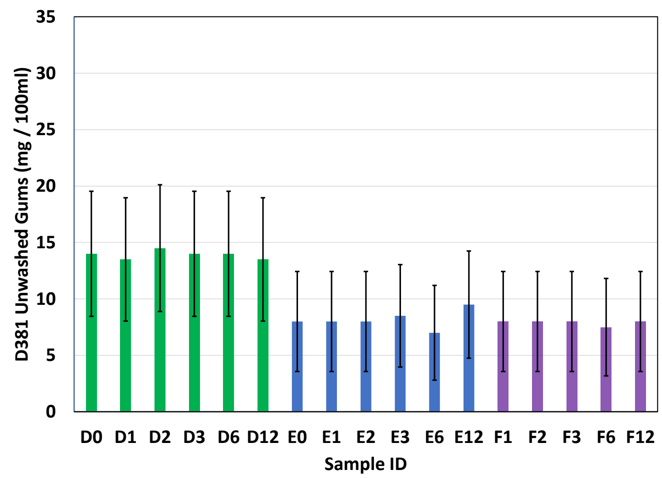

Figure 7. Unwashed gum results from ASTM D381 for the fuel samples that did not contain aftermarket additives.

The D381 test results for the A, B, and C samples are shown in Figure 8. As was observed for the initial samples, these results show that the A and B samples contain higher levels of unwashed gums than any of the other samples. The level of unwashed gums when any of the three additives were used remained consistent during the aging period, as was also noted for the samples that did not contain additional additives. As with the samples that did not use aftermarket additives, these results demonstrate that no significant gum formation occurred during sample aging. Since the baseline sample did not exhibit gum formation during aging, there is not an opportunity for the aftermarket additives to improve this result. Hence, the additives did not provide a benefit in terms of gum reduction during aging.

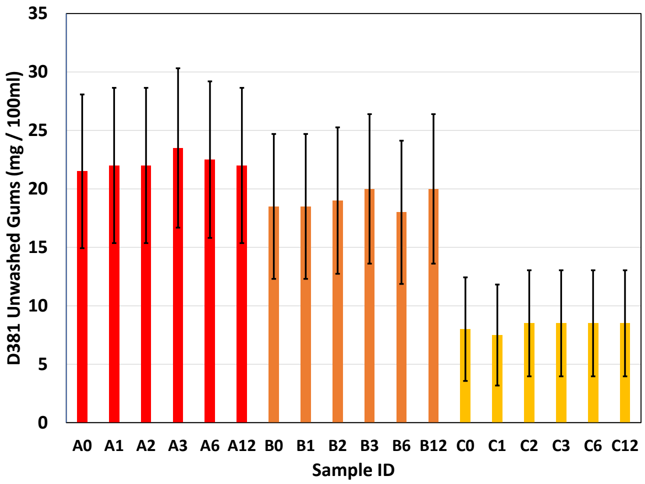

Figure 8. Unwashed gum results from ASTM D381 for the fuel samples containing aftermarket additives A, B, and C.

Oxidation Stability

The D7525 test was again used to assess oxidation stability for the gasoline samples during the aging period. The D, E, and F sample results are shown in Figure 9. Results for a series of samples were consistent within the stated reproducibility of the test. The E and F samples were self-consistent, indicating that there was not a significant difference in retention of oxidation stability between samples aged at ambient temperature and those aged in refrigeration.

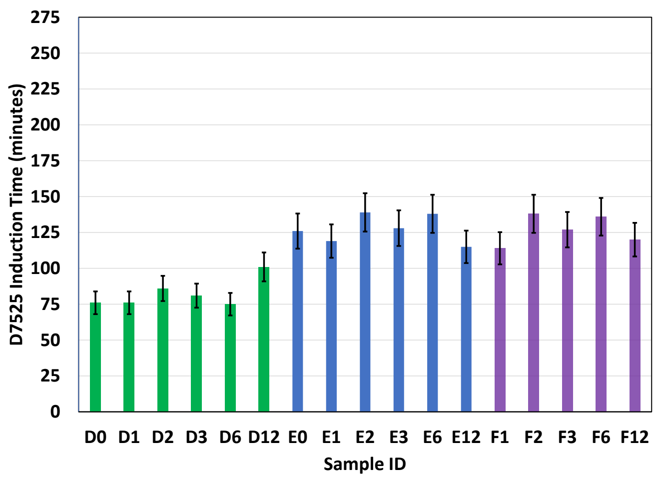

Figure 9. Oxidation stability for the D, E, and F samples during the aging period of 12 months.

The D samples also retained a consistent, but lower, level of oxidation stability during aging compared to the E and F samples. Oxidation stability results for the A, B, and C samples are shown in

Figure 10. Compared to the E samples, the A and B sample consistently demonstrate higher oxidation stability, with results of greater than 240 minutes. The C samples continue to provide oxidation stability that is similar to the E samples during the 12 month aging period.

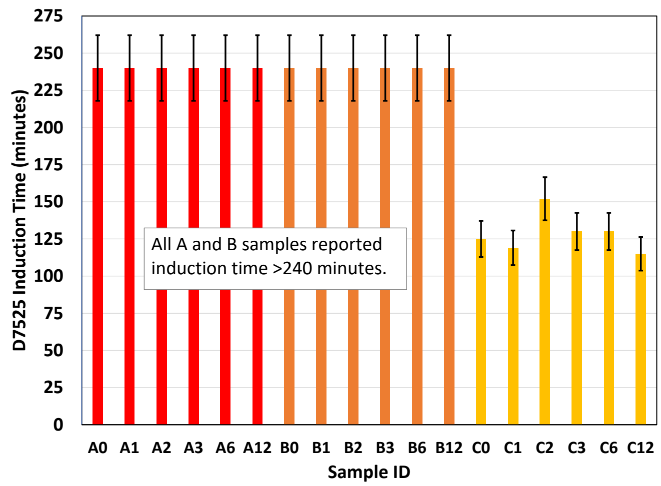

Figure 10. Oxidation stability for the A, B, and C samples during the aging period of 12 months.

These results show that there was no significant degradation of oxidation stability for any of the samples during aging. The D4814 specification for gasoline requires at least a 240-minute induction time but uses the less aggressive D525 test. [1] [9] This test was additionally performed on all samples for the 6 and 12 month aging periods. The results showed that all samples aged 6 and 12 months had greater than 1440 minutes of induction time. Therefore, all samples were compliant with gasoline specifications at 6 and 12 months of aging, regardless of whether an aftermarket fuel additive was used or not. Thus, although additives A and B do significantly improve oxidation stability, this added stability was not needed for the samples to remain within specification to at least 12 months of aging.

Gum Formation from Accelerated Oxidative Stressing

The results from the D381 test discussed previously quantify the gum content of the fuel samples during aging; the sum of the washed and unwashed gums from this test are known as existent gums. It is also possible to quantify the gums that may form if the sample is stressed by oxidation. ASTM D873 stresses the fuel samples under the same conditions used by D525 to measure oxidation stability, but additionally provides measurements of the mass of gums, both washed and unwashed, that result after this oxidative stressing. [10] The sum of the washed and unwashed gum masses from this test is referred to as the mass of potential gums. While the ASTM specifications for gasoline do not contain limitations on the gums formed from accelerated oxidative stressing, these results may nevertheless provide useful information. Figures 11 and 12 show the washed and unwashed gums that resulted from oxidative stressing of the fuel samples. In these plots the unwashed gums are shown as the solid bars. The washed gums are the open bars. The combination of both bars is the potential gum result for a given sample. The error bars are the published reproducibility values for potential gums.

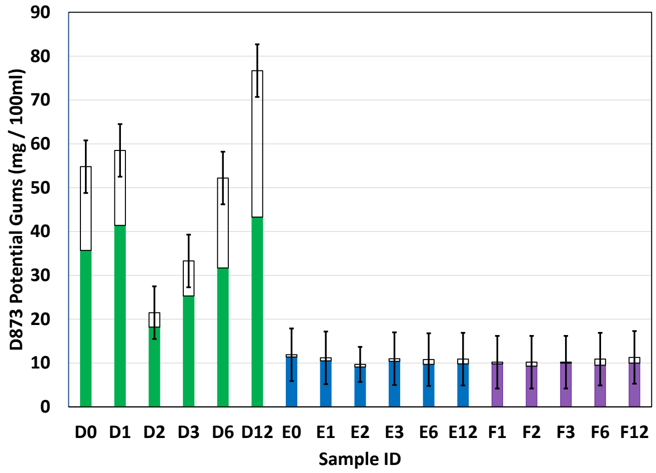

Figure 11. Potential gum formation as measured using ASTM D873 for the D, E, and F samples.

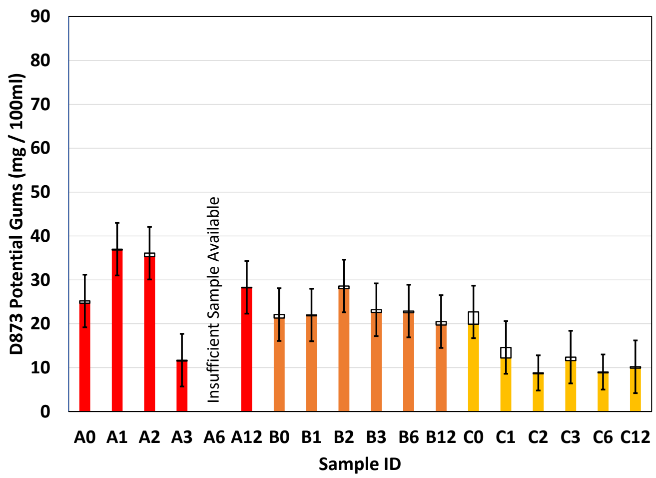

Figure 12. Potential gum formation as measured using ASTM D873 for the A, B, and C samples.

In all cases the potential gums exceeded the gums measured previously using the D381 test, though in most cases this increase was within the test reproducibility. The E and F samples continued to exhibit washed gum levels that were less than 1.4 mg/100ml in all cases and were the same within test reproducibility at all aging times. The A, B, and C samples also continued to exhibit low gum levels that agreed with the D381 unwashed gum results within the reproducibility of the test. These results show that oxidative stressing as conducted using the D873 protocol did not significantly increase solvent-washed gums for these samples.

Interestingly, the E samples exhibited high variability in potential gum formation and higher unwashed gum results than had been observed in the D381 results. The unusually high variability in these results makes drawing quantitative conclusions about these samples difficult. Qualitatively, the results indicate that this particular top tier fuel is more likely to form insoluble gums when oxidative stressing occurs. Top tier gasoline, as discussed previously, includes greater amounts of detergent additives that act to remove existing fuel and intake system deposits. It is unclear whether the increased insoluble gums noted under oxidative stressing could result in higher deposit formation for these samples under extreme conditions of fuel oxidation. The D381 results for these samples, however, clearly demonstrate that an aging period of 12 months under the conditions studied are not sufficient to result in higher unwashed gum formation for the top tier fuel.

Discussion of Results and Limitations of Study

The results of this fuel aging study show that the gasoline samples included in this study remained compliant with gasoline washed gum, oxidation stability, and copper corrosion specifications through 12 months of aging. Use of aftermarket fuel stabilizers was not required for the samples to remain compliant during this period. There was no significant reduction in oxidation stability over the aging period, suggesting that the samples could potentially have remained compliant with specifications for a longer period of time, or using an aging protocol with greater oxygen exposure.

Use of two of the aftermarket stabilizers (A and B) did significantly increase the oxidation stability of the gasoline samples as measured by ASTM D7525. This added oxidation stability could be beneficial if samples were aged long enough to deplete the antioxidants present in the baseline gasoline. The results of this study show that the baseline gasoline can resist oxidation for more than one year, hence, the benefit for using aftermarket additives would not arise until at least one year of aging, and likely longer.

The objective of this study was to investigate whether fuel aged in a sealed container under normal outdoor temperature conditions could benefit from the use of aftermarket stabilizer additives. It is important to note that this study only aged fuel in one way and that there are many other conditions in which fuel could be aged that were outside the scope of this study. For example, regularly opening the sample containers to simulate gradual use of fuel during extended aging might produce different results. Similarly, including gasolines that have higher olefin levels could reveal differing oxidation rates during aging. Finally, there are many more aftermarket additives available that could be included in a study such as this one. The results demonstrated with the three additives in this study may not be representative of all additives available to consumers.

Conclusions

- Gasoline samples studied did not exhibit signs of oxidation, gum formation, or corrosivity to copper during aging of up to 12 months under typical outdoor temperature conditions or when stored in refrigeration in sealed containers.

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- Three different aftermarket additives were studied; two resulted in significant gains in oxidation stability for the gasoline studied. These gains were not necessary for the baseline gasoline to remain compliant with relevant specifications for up to 12 months.

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Definitions/Abbreviations

ASTM	ASTM International
D130	Test for corrosiveness to copper
D381	Test for gum content
D525	Test for oxidation stability
D873	Test for potential gum formation
D4814	Specification for gasoline
D5191	Test for vapor pressure
D6730	Test for components of gasoline
D7525	Test for oxidation stability
DVPE	Dry vapor pressure equivalent
EV	Electric vehicle
PHEV	Plug-in hybrid electric vehicle