The ASTM Copper Strip Corrosion Test: Application to Propane with Carbonyl Sulfide and Hydrogen Sulfide

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Carbonyl sulfide (COS), which occurs as an impurity in commercial sources of propane, can hydrolyze in the presence of water to form hydrogen sulfide (H₂S) and carbon dioxide (CO₂). All commercial and HD-5 grade propane is required to pass the copper strip corrosion test, ASTM Test Method D 1838. While it is known that hydrogen sulfide will cause the failure of the copper strip test, it is widely believed that the hydrolysis of carbonyl sulfide can also cause the failure of the corrosion test. We have tested gravimetrically prepared mixtures of COS and H₂S in pure and commercial grade propane with a variant of the ASTM copper strip corrosion test. Minor changes to the published ASTM corrosion test were implemented for diagnostic or monitoring purposes in making the measurements. Surprisingly, mixtures containing as much as 1000 ppm (mass/mass) COS did not cause a failure of the test, even when the copper strip was in contact with the COS mixture for 2 h (double the normal contact time). Mixtures containing H₂S caused the failure of the test; however, concentrations as high as 3.5 ppm (mass/mass) H₂S passed the test. Moreover, we were not able to produce the colors and patterns shown on the ASTM copper strip corrosion standards lithograph.

Introduction

Carbonyl sulfide, (COS or S=O=C, CAS: 463-58-1), is a gas that is present in minor amounts in petroleum and coal refinery gases and, to a greater extent, in coal gasification streams. This material occurs as an impurity in commercial sources of propane (referred to as liquefied petroleum gas, LPG, available as commercial or HD-5 grades), and can hydrolyze in the presence of water to form hydrogen sulfide (H₂S) and carbon dioxide (CO₂). While COS is not itself corrosive, the hydrolysis product H₂S is corrosive, especially in the presence of water. Because propane and carbonyl sulfide have relatively similar normal boiling temperatures (−42.1 °C for propane, −50.2 °C for COS), approximately 90% of petrochemical COS will be found in the propane fraction of refinery gases. Only 10% will be found in the ethane fraction, while virtually none will be found in the butane fraction. It is not unusual to find up to 200 ppm (mass/mass, g COS/10⁶ total g) COS in the propane refinery gas fraction. Carbonyl sulfide also occurs in natural gas, and reports of COS in downstream natural gas are increasing. Natural gas is usually saturated with water at the well head, and much of the COS that is present is hydrolyzed to H₂S before processing.

The corrosivity of certain sulfur species in fuel gases such as LPG is determined by failures in the Standard Test Method for Copper Strip Corrosion by Liquefied Petroleum (LP) Gases, ASTM D 1838.4,5 In this test, a strip of deaned, polished copper is suspended in a vessel that has been rinsed with water, and pressurized with an appropriate quantity of LPG. The filled vessel is then maintained at 38 °C (100 °F) for 1 h, after which the strip is removed and immediately “read”. Reading a copper strip is done by comparison with lithographed standard strips provided by ASTM. The lithographs are divided into five classifications (Table 1). First, a pristine, freshly polished strip is displayed on the ASTM lithograph. This pristine strip does not have a rating or classification beyond “freshly polished”. Next, four subdivided levels of progressive sulfur-related corrosion are presented: level 1 (with 1a and 1b slight tarnish), level 2 (with 2a–2e moderate tarnish), level 3 (with 3a and 3b dark tarnish), and level 4 (with 4a–4c severe corrosion). For commercial LPG or HD-5 quality propane samples, 1a and 1b are considered passing, while anything higher is considered failing. LPG batches that fail the copper strip corrosion test must be reprocessed, or down-graded to a lower value product, thus resulting in a loss for the producer and additional costs for the consumer.

Engineering literature indicates that a COS concentration of 58 ppm (mass/mass) will cause failure of the copper strip corrosion test, with the presumed mecha-
nism being hydrolysis of COS to H₂S. It has also been observed that a tank car of LPG will pass the copper strip test in the morning, but fail the test in the afternoon after sitting in the sun for several hours. One author has reported a passing sample of LPG failing the copper strip test less than 30 min later. Here again, the presumed mechanism is COS hydrolysis. It should be noted that many basic compounds will also tarnish a copper strip, even in the absence of sulfur.

Since the development of the corrosion standards, several researchers have conducted studies to correlate the corrosion classifications with the actual quantity of sulfur and sulfur compound contamination in the petroleum product. Matthews and Parsons prepared corroded copper strips of various classifications by exposure to naphtha and kerosene containing elemental sulfur and mercaptans, and then analyzed the corroded surface of the copper using chemical analysis and cathodic reduction.11 Kashima and Nose related test strips corroded by sulfuric paraffin with the electron diffraction patterns of the copper oxide and copper sulfide films responsible for the corrosion classifications.12 More recently, the sulfur content of corroded surfaces was correlated with both the ASTM classification and the sulfur content of naphtha mixtures containing sulfur, mercaptans, disulfides, and organosulfides.13–16 Only two studies have focused on interpreting the copper strip test for lighter hydrocarbons. In the late 1970s, Pyburn et al. exposed copper strips to known concentrations of hydrogen sulfide and elemental sulfur in LPG and correlated ASTM corrosion classifications directly with sulfur concentration.17,18 In 1991, Clark and Lesage tested pentane solutions containing elemental sulfur, H₂S, COS, and other sulfur compounds as a model for LPG corrosion, yet their results in the heavier hydrocarbon did not duplicate those of Pyburn.19

### Experimental Section

#### Sample Preparation

To assess the potential failure mechanisms that might play a role in the copper strip corrosion test, we prepared a series of mixtures under controlled conditions. These mixtures contained only the pure compounds of interest, to eliminate possible side reactions or competing effects. The only departure from this protocol involved experiments that were performed with commercial propane.

Mixtures of COS or H₂S in propane were prepared gravimetrically. All samples contained 50 g of propane plus the quantity of COS or H₂S necessary to make the desired concentration. The mixture concentrations ranged from 500 to 1000 ppm (mass/mass) for the COS mixtures and 3.5 to 500 ppm (mass/mass) for the H₂S mixtures. Mixture preparation involved the cleaning and evacuation of a 475 mL sample cylinder, and mass additions of the components measured to ±1 mg. Mixture cylinders were allowed to reach thermal equilibrium before the mass was recorded. The uncertainty in the mass (measured with an electronic load cell) resulted in an uncertainty in the COS mixture concentrations of ±2%. It was not possible to directly prepare the lower concentration H₂S mixtures with the same uncertainty, because the mass of H₂S required was below or near the uncertainty of the balance. The 3.5 to 100 ppm (mass/mass) H₂S mixtures were thus prepared by serial dilution from a 2.5 mass percent mixture of H₂S and propane (all components were gas phase). The resulting uncertainty in concentration for the lowest concentration (3.5 ppm (mass/mass)) H₂S mixture prepared from this stock mixture was ±13%. Sample cylinders were constructed of carbon steel, and all valves, fittings, and tubing were 316 stainless steel (AISI designation). Ultra high purity propane (99.7%), COS (99%), and H₂S (99.5±%) were obtained from commercial vendors, and their purity was confirmed by gas chromatography. Commercial grade, odorized propane was purchased from a consumer filling station and was used as received. To assess the reproducibility of the test method, duplicate mixtures were prepared and corrosion-tested for the ultra high purity samples of 500 and 1000 ppm (mass/mass) COS and 3.5 ppm (mass/mass) H₂S.

#### Corrosion Testing Apparatus

The apparatus used for the copper strip corrosion test was made from a sight glass.

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gauge equipped with a type 316 stainless steel body, and capable of operation to 8.3 MPa (1200 psig) at 38 °C (100 °F) (Figure 1). The sight glass gauge was used instead of the commercial vessel proposed by ASTM guidelines in order to allow observation of the liquid level in the filled container. A type 316 stainless steel pipe plug at the bottom of the sight glass gauge was fitted with a length of type 316 stainless steel rod terminated in a hook, upon which the prepared copper strip was suspended. The apparatus was furnished with a manifold to allow filling, evacuation, and venting. A well-stirred water bath (sized with a favorable filling factor to accommodate the sight glass gauge) maintained at 38 °C (100 °F) provided temperature control for the test. Between each test, the sight glass gauge was thoroughly cleaned and the final rinse was done with distilled, deionized water.

Testing Method. Copper strip corrosion testing of the standard mixtures adhered closely to ASTM guidelines. The tests began by polishing and cleaning a copper strip (70 mm × 12.5 mm × 3 mm) according to ASTM guidelines, by use of silicon carbide grit paper of varying degrees of fineness and acetone as the wash solvent. Electrolytic tough pitch copper of high purity was used for all tests. A milliliter of distilled, deionized water was added to the sight glass gauge, swirled to coat the walls, and then drained from the vessel. The freshly prepared copper strip was then suspended from the hook on the vessel plug, and inserted into the bottom of the vessel. The vessel was evacuated to 0.13 Pa (10⁻³ mmHg), and the sample was introduced through the manifold. The sample was verified to completely submerge the copper strip by observation through the sight glass. No external light source was used to illuminate the sight glass during a test; the test was conducted with only minimal exposure to ambient light. The loaded gauge was then submerged in the 38 °C bath for 1 h. At the end of the time period, the vessel contents were vented, and the copper strip was removed and interpreted by comparison against the ASTM copper strip corrosion standards. Digital photographs were recorded of the pristine copper strip, the “before” image, and the exposed strip, the “after” image. Moreover, the spent copper strips were coated with a layer of polyurethane and stored in a dark location as an archive.

As an independent blind review of our copper strip “readings”, three engineers who work in the LPG industry and routinely conduct the copper strip test were shown images of our copper strips after exposure to various COS or H₂S propane mixtures. The individuals were asked to interpret the copper strips without knowledge of our test conditions, or knowledge of our conclusions. In all cases, their interpretation of the results exactly matched our own.

In addition to the experiments that adhered strictly to the ASTM procedure, we conducted several experiments in which the procedure was intentionally varied. The first variation was to keep the test vessel in the water bath for double the ASTM mandated time, or 2 h, to determine how longer test residence times would affect the corrosion results. In the second variation, we allowed for a separate water phase to be in contact with the copper strip during the test, to assess how a wet LPG sample would influence the test results. For these experiments, the vessel containing the pristine copper strip was evacuated, and either 5 or 20 mL of distilled water was added to the vessel, then the propane sample was added to the vessel to form a condensed propane layer on top of the water layer (in vapor–liquid–liquid equilibrium). The vessel was immediately placed into the water bath. No attempt was made to mix the phases.

Results

The copper strip corrosion test was performed on mixtures of COS in both ultra high purity propane and commercial grade propane. Commercial grade propane was examined to assess how the lower purity product would influence corrosion. Finally, mixtures of H₂S and propane were tested to quantify how much H₂S was necessary to produce a corrosion test failure.

Copper Strip Corrosion Tests on COS + Propane. To determine the amount of corrosion caused by COS in propane, test mixtures were prepared with 500, 750, and 1000 ppm (mass/mass) COS and ultra high

purity propane. Samples of the ultra high purity propane (with no added COS) were also subjected to the corrosion test. Figure 2 represents the before and after images of the COS + propane mixtures, and Table 2 summarizes our interpretation of corrosion levels. The pure propane produced a copper strip indistinguishable from the freshly polished strip. The copper strip exposed to the 500 ppm (mass/mass) mixture was also recovered unchanged from the pristine strip, and therefore was rated “0” (actually not ratable on the ASTM scale). For the 750 and 1000 ppm (mass/mass) mixtures, the copper strips were recovered from the test in a condition barely discernible from the pristine strip, and were given an ASTM 1a classification. Duplicate mixtures of 500 and 1000 ppm (mass/mass) COS were prepared and corrosion tested. There was no difference in test results for duplicate measurements. Additional mixtures of 500 and 1000 ppm (mass/mass) COS were tested for 2 h rather than the ASTM-specified 1 h. In both cases, the resulting copper strips were somewhat more tarnished than the strips from the 1 h test, with an ASTM classification of 1a for the 500 ppm (mass/mass) mixture and 1b for the 1000 ppm (mass/mass) mixture. In no case was a “failed” result obtained for a COS + propane mixture.

Tests were also performed on 500 and 1000 ppm (mass/mass) mixtures where 20 mL of water was added to the test vessel. For these experiments, there was more corrosion present on the copper strip; however, neither of the concentrations produced more than an ASTM 1b rating (Figure 3). Our study of the COS hydrolysis reaction rate supports this observation, in which we found that the rate of COS hydrolysis is proportional to the quantity of water present. It is therefore not surprising that more corrosion is observed under test conditions in which more water is present. In these experiments, the water covered the lower 2/3 of the copper strip. It is interesting that the majority of the corrosion occurred above the water phase, in the propane phase. This observation was unexpected, since any appreciable H₂S that formed from the hydrolysis

Table 2. Corrosion Classification and Test Results for COS in Ultra High Purity Propane (UHP) and Odorized Commercial Grade Propane (LPG)

<table>
<thead>
<tr>
<th>sample (ppm (mass/mass))</th>
<th>ASTM rating</th>
<th>result</th>
</tr>
</thead>
<tbody>
<tr>
<td>UHP, no COS added</td>
<td>0</td>
<td>pass</td>
</tr>
<tr>
<td>500 ppm COS in UHP</td>
<td>0</td>
<td>pass</td>
</tr>
<tr>
<td>750 ppm COS in UHP</td>
<td>1a</td>
<td>pass</td>
</tr>
<tr>
<td>1000 ppm COS in UHP</td>
<td>1a</td>
<td>pass</td>
</tr>
<tr>
<td>500 ppm COS in UHP, 2 h test</td>
<td>1a</td>
<td>pass</td>
</tr>
<tr>
<td>1000 ppm COS in UHP, 2 h test</td>
<td>1b</td>
<td>pass</td>
</tr>
<tr>
<td>500 ppm COS in UHP, 20 mL H₂O</td>
<td>1b</td>
<td>pass</td>
</tr>
<tr>
<td>1000 ppm COS in UHP, 20 mL H₂O</td>
<td>1b</td>
<td>pass</td>
</tr>
<tr>
<td>LPG, no COS added</td>
<td>1a</td>
<td>pass</td>
</tr>
<tr>
<td>600 ppm COS in LPG</td>
<td>1a</td>
<td>pass</td>
</tr>
<tr>
<td>1000 ppm COS in LPG</td>
<td>1a</td>
<td>pass</td>
</tr>
<tr>
<td>600 ppm COS in LPG, 5 mL H₂O</td>
<td>1a–1b</td>
<td>pass</td>
</tr>
<tr>
<td>600 ppm COS in LPG, 20 mL H₂O</td>
<td>1b</td>
<td>pass</td>
</tr>
</tbody>
</table>
of COS during the test would be expected to have had greater affinity for the aqueous phase.

For the studies with commercial (odorized) propane, the corrosion test was initially performed on the propane "out of the bottle" with no added COS. Unlike the ultra high purity propane, commercial propane produced some slight tarnish, giving a rating of 1a on the ASTM scale. Mixtures containing 600 and 1000 ppm (mass/mass) COS in commercial grade propane were tested and both mixtures produced strips with class 1a tarnish, which were indistinguishable from the commercial propane-only sample (1000 ppm (mass/mass) result is shown in Figure 2). Two additional 600 ppm (mass/mass) mixtures were tested with varying quantities of water. In the first experiment, 5 mL of water was added to the vessel to generate a water level just below the base of the strip. The resulting strip was slightly darker than in the trace water test, and was classified between 1a and 1b. In the second experiment, 2/3 of the strip was submerged in 20 mL of water. The submerged portion of the strip was significantly darker orange than the unsubmerged portion, indicative of class 1b tarnish. There seemed to be a silvery tone to the unsubmerged portion of the copper strip, which may have been indicative of a class 2d tarnish; however, the subjective nature of this test makes absolute interpretation impossible. Despite the somewhat more dramatic results obtained when preparing mixtures in commercial propane, in no case was an unambiguous failure classification obtained.

Copper Strip Corrosion Tests on H₂S + Propane.

On the basis of the reports in the literature, one would have expected moderate concentrations (50 to 100 ppm, mass/mass) of COS in propane to cause copper strip corrosion test failure. When we could not produce a copper strip test failure under any conditions with COS mixtures, we tested standard mixtures of H₂S in ultra high purity propane to confirm the validity of the corrosion test. By measuring H₂S propane mixtures over a wide concentration range, we attempted to reproduce the various levels of tarnish shown on the ASTM copper strip corrosion standards to quantify how much H₂S is necessary to cause the various classifications of corrosion. Before and after images are shown in Figure 4. Duplicate 3.5 ppm (mass/mass) H₂S mixtures were prepared and tested. Test results were identical for the two mixtures and the result for one of the 3.5 ppm (mass/mass) mixtures is shown in Figure 4. While the severity of corrosion does indeed increase with increasing H₂S concentration, it was impossible to interpret the majority of our results within the accepted classifications of the corrosion standards. In fact, many of the results we obtained did not resemble any of the litho-

graphs. The 13, 25, and 50 ppm (mass/mass) H₂S mixtures appeared to produce similar results, despite the progressive increase in H₂S concentration. More remarkable was the fact that 100 and 500 ppm (mass/mass) mixtures did not completely corrode the copper. We could not even cause an ASTM 4c level classification by filling the moistened vessel with pure H₂S at 1.55 MPa (225 psig)! While these results clearly demonstrate a limitation of the copper strip corrosion test, the single most disturbing result is that our 3.5 ppm (mass/mass) mixture of H₂S in propane passed the copper strip test with a 1a classification. LPG with this level of H₂S would not generally be considered merchantable.

Discussion

The results of all of our copper strip corrosion testing are clearly contrary to previously reported results, and contrary to conventional wisdom, which holds that much lower concentrations of COS should cause failure of the copper strip corrosion test.

The copper strip corrosion tests that were performed in this research indicate that the hydrolysis of COS is too slow to account for test failure with propane. This result, at first glance, is somewhat surprising given the magnitude of the industrial difficulty that this reaction is thought to cause. Recall that plant operators and processors expect corrosivity problems when the COS concentration is approximately 50 ppm (mass/mass).8 In our studies, mixtures of COS in propane were never observed to fail the copper strip corrosion test, even at 1000 ppm (mass/mass), a COS level which, in LPG, would be considered massive. In fact, our copper strips never extended beyond a 1a classification unless we doubled the test time or added copious quantities of water to the test vessel. Even in these cases, a “pass” was recorded.

The inability of COS to cause LPG corrosion failure is supported by our own measurements of the kinetics of the COS hydrolysis reaction in propane.9 In 1 h, the hydrolysis reaction is simply too slow at 38 °C to produce the quantity of H₂S necessary to fail the copper strip test. Regardless, it has been suggested that the very low levels of H₂S required for corrosion test failure, 0.35 to 1 ppm (mass/mass), are produced even by slow hydrolysis.6,8,17 By contrast, our results indicate that concentrations of H₂S up to an order of magnitude higher will pass the corrosion test with only a 1a rating. It is indeed noteworthy that we could not produce the standard ASTM corrosion classifications with high purity mixtures of H₂S and propane.

It is apparent from this work that the presence of COS alone, even at relatively high concentrations, and even
in wet propane, is not enough to cause the repeated failure of the copper strip corrosion test as practiced in the LPG industry. While we by no means advocate the sale of high COS level LPG, it is clear that COS is not the sole cause of failure. It is probable that the copper strip corrosion test failures that are experienced in the field are caused either by a combination of sulfur species being present, or by an as-yet-unidentified agent. There are measurements and anecdotal evidence to support the former explanation. Situations are reported in industry in which two separate batches of LPG pass the copper strip corrosion test individually, but when the two batches are combined, the mixture fails. This can happen if one batch has a trace of H2S, and the other has a trace of elemental sulfur. The components can then act synergistically when mixed to produce the unacceptable corrosion test result. Catalytic surfaces such as iron oxides and iron sulfides, which can be found in LPG transport and storage vessels, may account for corrosion test failure as these materials can generate elemental sulfur in the presence of H2S.

Conclusions

We have examined the ASTM D 1838 copper strip corrosion test for LP gases and have found that contrary to popular opinion, the hydrolysis of COS is not fast enough to cause failure of the copper strip test. Moreover, COS levels as high as 1000 ppm (mass/mass) in propane will not tarnish a copper strip beyond a 1a ASTM classification. H2S levels as high as 3.5 ppm (mass/mass) in propane will not cause copper strip test failure. Finally, using standard mixtures of H2S in propane ranging in concentration from 6 to 500 ppm (mass/mass), we were not able to produce the various

Figure 4. Post-corrosion test images of copper strips (sides 1 and 2) are shown after exposure to mixtures with H2S concentrations (ppm, mass/mass) from top: 0, 3.5, 6, 8, 13, 25, 50, 100, 500, pure H2S.
classifications of the ASTM copper strip corrosion standards lithograph. We believe that additional work is necessary to better define the conditions under which sulfur compound synergy can affect the copper strip corrosion test. We further believe that additional work should be done to improve the concept and practice of the test itself.

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