B20 to B100 Blends as Heating Fuels

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Exposure of "Yellow Metals" at Low Temperature

There is considerable prior published research that demonstrates that exposure to copper can accelerate the oxidative degradation of fuels including No. 2 fuel oil and biodiesel, which can result in the formation of sludge and sediment. The ASTM D975 standard for on/off road diesel states, "Copper and copper-containing alloys should be avoided. Copper can promote fuel degradation and can produce mercaptide gels. Zinc coatings can react with water or organic acids in the fuel to form gels that rapidly plug filters." It goes on further to state, "The formation of degradation products can be catalyzed by dissolved metals, especially copper salts. When dissolved copper is present it can be deactivated with metal deactivator additives." In general, copper is not recommended for either distillate fuel oils or for biodiesel due to these factors.

In oil-fired home heating systems, however, copper fuel lines are commonly used due to their lower cost and ease of manipulation and installation. Most installations in the United States are "one-pipe" systems where fuel flows from a steel tank, through copper lines, through a fuel filter, to the burner's pump. Between the pump and the nozzle, copper lines are again commonly used. Fuel nozzles are either brass or stainless steel and could provide the opportunity for fuel to be exposed to yellow metals (i.e. those containing copper) at higher temperatures. This is addressed in the next, high temperature, section.

Some installations are "two-pipe" systems. In this case, the pump pressure regulator bypass flow returns to the fuel tank through a second copper line.

<u>Experimental</u>

When the burner is in regular operation, the residence time of the fuel in the copper line is short. The most significant opportunity for long exposure times is during the summer shut-down of an oil-fired appliance which is used for heat only, such as a warm air furnace. Combination appliances which also provide domestic hot water would run in the summer as well. In this project, a study was done of the impact of such a long-term storage in copper tube. A set of tubes, each 10 inches in length, was assembled in a holder with a vertical orientation. Table 3-1 details the metals used in the exposure test. Each tube was filled and this system idle at ~ 21 °C (70 °F) for six months. Figure 3-1, below, provides an image of the tube arrangement for the six-month period. Two of these assemblies were used in the test. For each of these the following test matrix was used:

Table 3-1 Test Matrix in Long-Term, Room Temperature Metal Exposure Test

	B0	B20	B100
Stainless Steel	X	X	X
Old Copper	X	X	X
New Copper	X	X	X

In one of the two test assemblies conventional No. 2 fuel oil with approximately 1500 ppm sulfur was used. In the other ultralow sulfur diesel (ULS) with sulfur below 15 ppm was used as the base fuel.

The old copper was a fuel line which had been in service for around 30 years. Over such a long time, it could be expected that the inner surface of the copper tube might become passivated which could reduce the interaction between the metal and the bulk fuel.

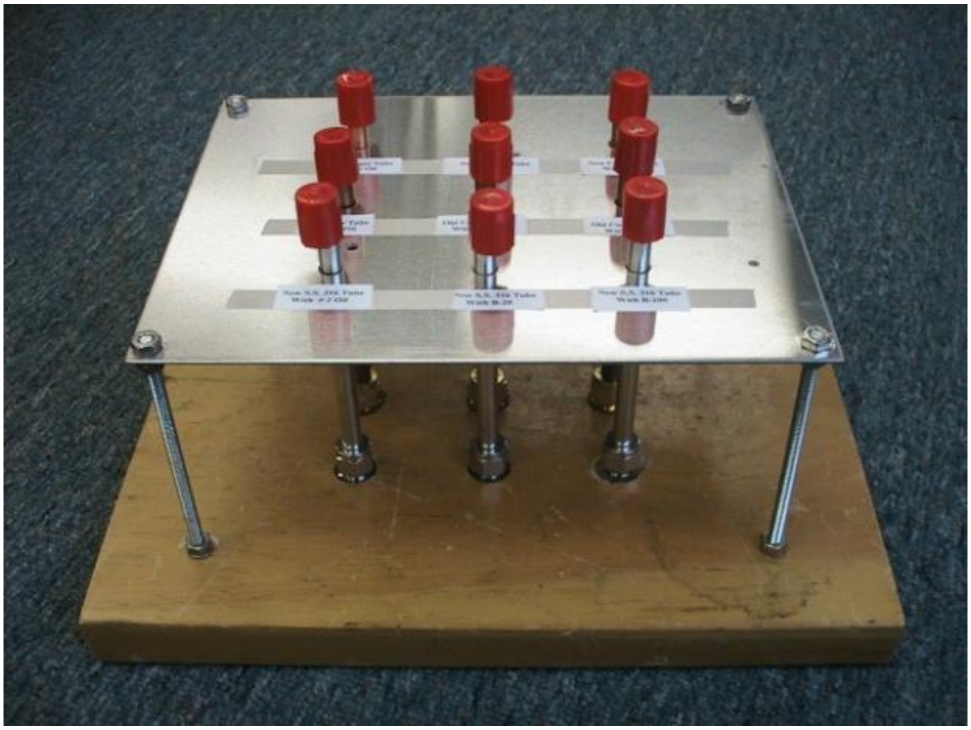

Figure 0-1 Photo of long term, low temperature metal exposure test.

Results

Figure 3-2, provides the measured acid numbers after the completion of the six-month period for the conventional, 1500 ppm No. 2 fuel oil. Results with the ultra-low sulfur diesel samples were similar.

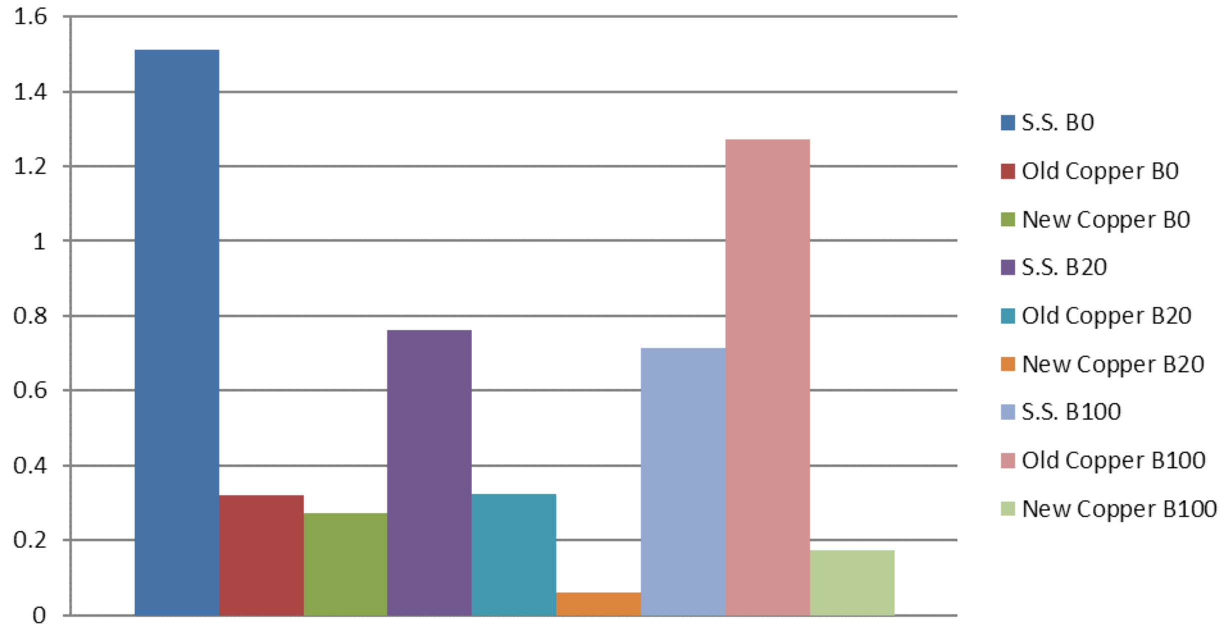

Figure 0-2 Acid numbers of the test fuels after the six-month period

The starting acid number for the fuel were approximately 0.4. Overall, this shows results for the biodiesel blends were comparable or lower to that of B0 soaked in stainless steel, and that samples soaked in copper did not lead to increased acid number versus stainless steel. For the stainless-steel samples, for the B0 and B20 fuels did have higher acid number at the end of the test than the copper samples, although all were below the acid value of 2 which was shown in bench testing to have potential effects on elastomer properties. For B100 the stainless-steel results were mixed between the stainless steel and new and old copper.

Discussion

One possible explanation for these results is that acids, produced during the long-term storage complex with the copper and are effectively neutralized. It should also be noted that these containers were sealed limiting the diffusion of oxygen to the fuel. This is similar to the situation that would exist in the fuel lines during a long summer shutdown. Overall, however, these results do not indicate a strong concern with copper in this case or differences for the biodiesel blends outside those generally observed with B0. We postulate the controls in the most recent, updated version of the B100 ASTM standard D6751 for acid number and oxidation reserve contributed significantly to these results, as there are no current controls in conventional fuel oil for acid number or stability.

Some of the copper tubes were cut open for inspection of the internal surface. Figure 3-3, below, provides a comparison of the appearance of the “new” copper tubes after the exposure period. All of the tubes examined illustrated no damage, interaction with the fuel, or fuel degradation deposits. Both samples show some particulate deposits simply from the cutting operation. This result is consistent with the ASTM copper strip corrosion test which all these fuels are required to pass.

Heating oil

B-20 blend

Figure 3-3 Photos of internal surfaces of "new" copper tube after the six month exposure period.

<u>Conclusions</u>

These tests were conducted at low temperatures, simulating summer shutdown of a heat-only boiler or furnace. The test results showed no obvious impact on the copper tubing used as a reactor vessel in this test. The results also showed that the end-of-test acid number for the samples exposed to copper was not higher than for the samples stored in stainless steel. In two of the three samples the acid number for the copper stored samples was significantly lower than for the samples stored in stainless steel tubes.