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Potential Problems of High Efficiency Fuel Filtration and Cold Flow Improver Additives

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Abstract

Cold flow improvers are a class of fuel additives designed to modify the size, shape, and number of wax crystals that form fuels below their cloud point. These additives are designed to precipitate at temperatures above the fuel's cloud point and serve as both nucleation centers and wax particle growth arresters. In this study we demonstrate that, under certain conditions, current commercial cold flow improvers formulated with poly(ethylene-co-vinyl acetate) can directly lead to premature fuel filter plugging. Furthermore, the necessary use of high efficiency filtration to protect modern high-pressure common rail fuel injection systems exacerbates these problems. High efficiency filters tend to capture the wax particles, even those modified with cold flow improvers, that would pass through the more open filters previously used to protect fuel systems.

Introduction

The past fifteen years have brought tremendous change to the U.S. and worldwide diesel fuel industry. Three primary changes that affect the usage of fuel are increased engine emissions regulations, biodiesel mandates, and refinement of fuel to ultralow sulfur diesel (ULSD). Each of these changes has forced adaption through both mechanical and chemical technologies to achieve compliance with government regulations.

The first of these changes, increased engine emissions regulations, has been dealt with by engine manufacturers through the usage of high-pressure common rail fuel system and exhaust treatment technologies. The fuel systems for high-pressure common rail engines rely on fuel injectors with significantly tighter clearances compared to previous designs. The tighter injector clearances have forced the need to filter fuel to levels of efficiency never before encountered in

fuel applications. Typical cleanliness demands for fuel delivered to injectors is in the range of 12/9/6 per ISO 4406. For an incoming fuel of code 18/16/13 this means that the fuel filtration system must remove up to 99.2% ($\beta=125$) of particles $\geq 4 \mu\text{m}$.

The second two diesel fuel changes have altered the composition of the fuel, forcing both fuel refineries and additive manufacturers to face a new set of chemistry related challenges. The increased usage of biodiesel has added several new chemicals to diesel fuel. The majority of biodiesel is fatty acid methyl esters (FAMES) along with limited amounts of glycerin, alkyl glycerides, sterol glucosides, and fatty acids. These chemical additions have occurred as other compounds have been removed with the switch to ULSD. Hydrotreatment of diesel fuel feedstocks to remove sulfur and other heteroatoms not only changes the combustion and emissions properties of the fuel, but also the inherent lubricity. Fuel lubricity is helpful to minimize wear of metal to metal contacts in fuel injectors and pumps. Several surfactant additives such as alkyl esters, carboxylic acids, and amides are used to replenish the lubricity lost with ULSD.

It is undoubted that new fuel systems and fuel chemistry changes have led to less harmful exhaust emissions. However, the combination of unintended precipitation of fuel and additive components along with the necessity of high efficiency filtration has led to a “perfect storm” leading to a high occurrence of premature fuel filter plugging. In the past few years, Donaldson scientists analyzed hundreds of fuel filters that were plugged before reaching their expected end of life. Filter analysis was performed on products from all major manufacturers and spanned an array of efficiencies and fiber chemistries. Regardless of filter construction it was found that a few unique chemistries are repetitively identified as the sole reason for an individual acute filter plugging event. In this report we detail a common cold flow improver (CFI) chemistry, poly(ethylene-co-vinyl acetate) (EVA), that can precipitate from ULSD and cause premature plugging of high efficiency fuel filters.

Cold flow improvers are a class of fuel additives that work to improve low temperature operability by keeping fuel filterable below its cloud point.¹ These additives work by being only moderately soluble in ULSD. As diesel fuel cools, solubility of the polymeric EVA molecules decreases and precipitation occurs. The temperature range over which precipitation occurs is broad and typically spans above and below the cloud point of the fuel. The broad range of temperature dependent solubility allows for two useful mechanisms for CFIs.

The first mechanism is that polymer particles that precipitate above the cloud point of the fuel act as nucleation centers for wax crystals. Instead of waxes forming a small number of very large (100-200 μm) particles, nucleation centers force formation of a larger number of smaller particles. The second mode of action is that polymers precipitated below the cloud point are incorporated into the wax particles and allow for modification of particle shape. Cold flow additives typically make finger/rod shaped particles as opposed to flat plates formed without additive.

The usefulness of a CFI additive is typically measured using a cold filter plugging point (CFPP) test such as ASTM D6371. In this test 20ml of fuel is repeatedly drawn through a 45 μm mesh screen at increasing cold temperatures. The temperature at which 20ml is no longer able to pass through the screen in 1 minute at 2 kPa is recorded as the CFPP.

Results and Discussion

This report documents two unintended consequences of the limited solubility of polymeric CFI additives in diesel fuel. These two problematic scenarios can result in increased pressure drop and potential premature plugging of high efficiency fuel filters. The first of these scenarios is that during additive manufacturing and blending, the EVA feedstock is never fully dissolved into the additive package. This results in insoluble, and often highly crystalline, particles being present at room temperature in the distributed product. Fortunately, proper manufacturing techniques can ensure a fully solubilized and particle free additive package. The second scenario occurs regardless of how well the additive was manufactured and may be unavoidable with current EVA based CFI formulations. As noted above, one mode of action for CFIs is to have some limited solubility and precipitate particles above a fuel's cloud point. We find that high efficiency filtration, which is necessary to protect today's engines, is able to capture the pre cloud point particles causing an unexpected pressure increase.

Investigation into improperly manufactured EVA based CFIs was performed by evaluating the performance of 5 commercial off-the-shelf additives. These additives are referred to as samples A-E and were dosed according to manufacturer guidelines. Figure 1 illustrates plots of differential pressure as a function of time as 1 liter of fuel is continuously recirculated through a 47mm patch of filter media. The filter media has a nominal rating of 3 μm , an effective exposed area of 13.8 cm^2 , and was exposed to fuel at 190 ml/min at room temperature. This flow rate corresponds to a typical linear flow velocity of a bulk filtration application and 10 times the velocity of an on-engine filter application.

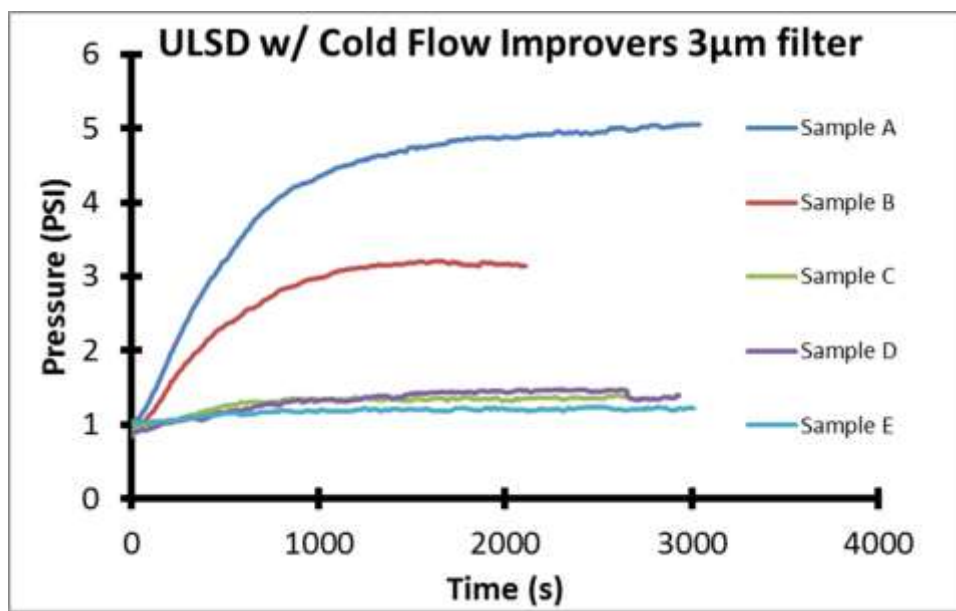


Figure 1. Differential pressure as a function of time for 5 samples of EVA based CFI added to ULSD.

In this experiment CFI was added to the fuel at the beginning of the test (time = 0). For two of the samples (A and B) we observe significant rise in the pressure across the filter. The rise in pressure decays over time as the fuel is cleaned in the multiple filter passes. Normalized by filter area and flow speed, the rise in pressure corresponds to 150 gallons through a typical full size bulk fuel filter element or 400 gallons through a typical on-engine filter. It is clear to see that this amount of increased pressure would severely limit the life of these filters. Additional testing has shown that this pressure increase can be avoided by switching to a less efficient filter media. However, this would also offer insufficient filtration against traditional damaging fuel contaminants such as dust/dirt particles

In order to determine why significant differences were observed for the 5 CFI samples several analytical chemistry methods were performed on the EVA polymers. All polymers samples had similar molecular weight distributions between ~1 and 20 kDa, as tested with size exclusion chromatography using polystyrene standards. Similarly, thermal gravimetric analysis demonstrated that all EVA samples had a constant ethylene to vinyl acetate ratio of ~0.3-0.4. We did determine differences in the dosage rates (100-500 ppm), but there were no trends in dosage rate relative to pressure drop. Without any clear chemical differences between the off-the-shelf CFI additives, the most likely reason for sample differences is variation in manufacturing quality.

We present two experimental justifications that support the hypothesis of additional pressure drop from some commercial CFIs being due to inadequate additive manufacturing. The first of these is microscopy analysis of the additive package. Figure 2 shows the observation of a strikingly large number of ~2-3 µm size particles in Sample A. These particles were present in the additive sample and did not dissolve into the fuel upon blending at room temperature. It was

found that transmitted polarized light gave the best imaging quality. Polarized light microscopy enhances contrast of birefringent materials. The birefringent properties of the EVA particles can be interpreted that the particles are either crystalline or have significant crystalline domains.

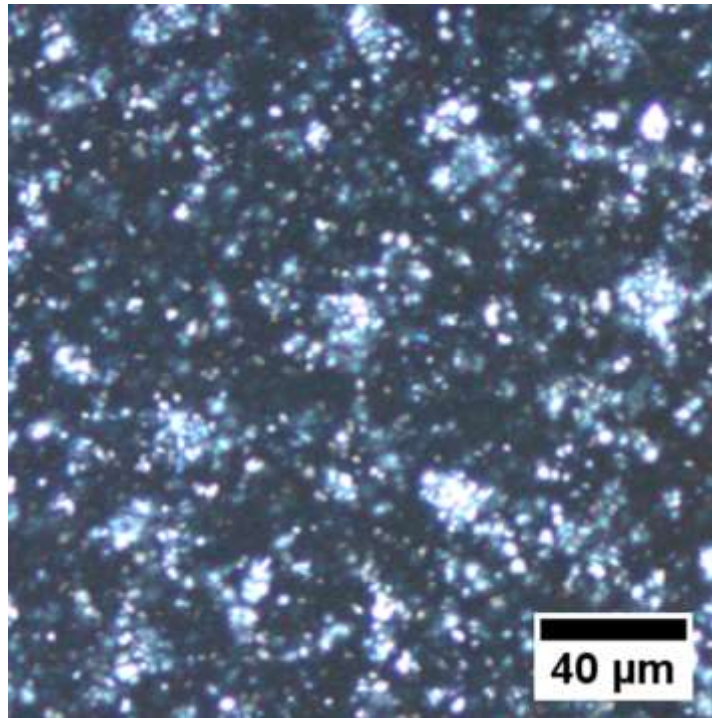


Figure 2. Transmitted polarized light microscope image of EVA based CFI sample A.

A second piece of experiment evidence supporting our hypothesis is found by investigating the thermal history of EVA in CFI additives. Figure 3 demonstrates the reduction in observed pressure increase with the addition of either sonication or thermal energy to the additive package. Once the EVA polymer molecules are solubilized into either the additive package or final blended fuel, they remain in fuel, at least at room temperature.

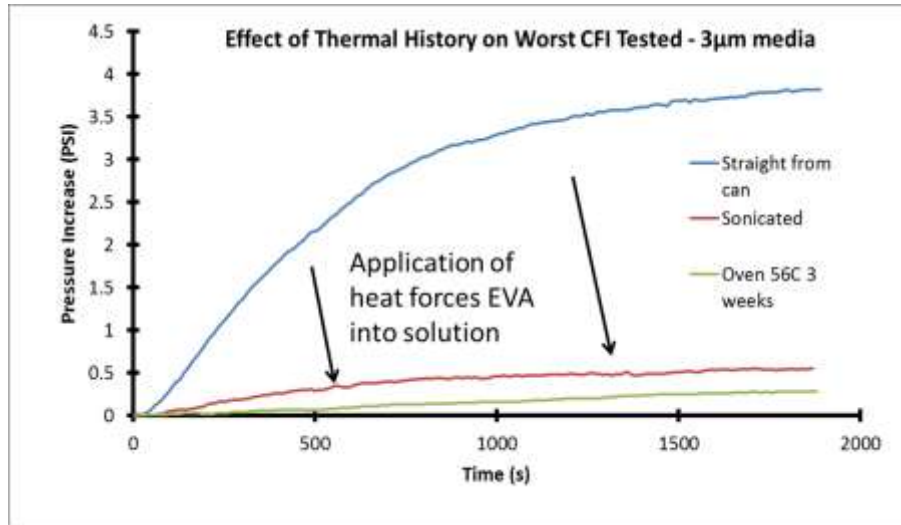


Figure 3. Differential pressure as a function of time for sample A. Experiments are shown for additive as received (blue), sonicated for 10 minutes (red), and held in an oven at 56°C for 3 weeks (green).

This data demonstrates that appropriate manufacturing protocols must be employed when initially dissolving EVA based polymers into the initial additive package. If the EVA is not initially fully solubilized, the residual particles can be captured on high efficiency filters causing premature plugging events. Simple application of heat during the dissolving process should be sufficient to avoid these problems.

As noted above, a second mode of premature filter plugging can occur at cold temperature when initially soluble EVA polymer can precipitate into particles. The broad temperature dependence of solubility inherent to polymers was tested by cooling additized fuel as it was continuously recirculated through a filter patch. Figure 4 demonstrates the differential pressure across filters as 1 liter of fuel is continuously recirculated through a 47mm patch of filter media. Similar to the experiment for Fig. 1, the filter media has an effective exposed area of 13.8 cm² and was exposed to fuel at 190 ml/s.

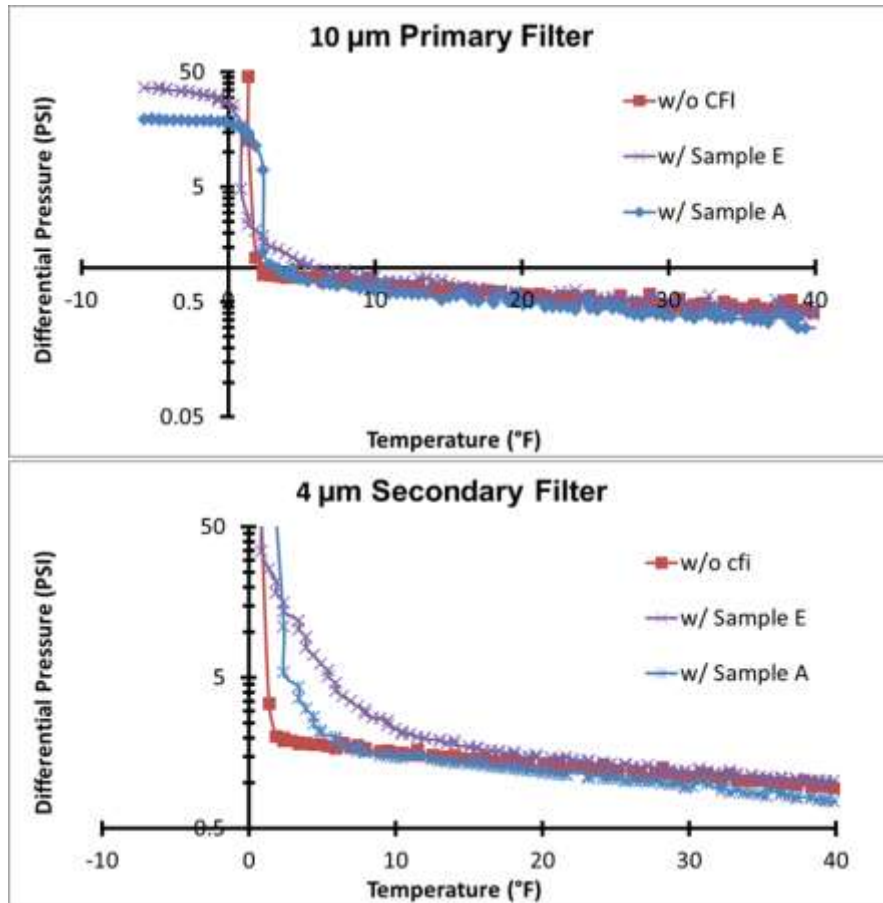


Figure 4. Differential pressure as a function of fuel temperature as measured for 10 μm (top) and 4 μm (bottom) nominal filter media. Fuel was tested as received (red) and with either Sample A (blue) or Sample (E) EVA based CFI.

In this experiment we tested the performance of two typical on-engine fuel filters. The top plot is for a 10 μm primary filter media and the bottom is for 4 μm secondary media. For each media the fuel was used unadditized and EVA based CFIs A and E. Note that the sample A additive was preconditioned by holding in an oven for 1 week at 60°C to fully dissolve the additive package in the original container. For each experiment the fuel and experimental apparatus was quickly cooled to 50°F and then cooled at 0.35°F/min. For simplicity, we can differentiate the analysis of each curve into two regimes. The division of these two regimes is the cloud point of the fuel, which was measured at 1°F per ASTM D2500.

As the fuel is cooled all samples exhibit an exponential increase in differential pressure from 50° to near 10°F. This pressure increase is attributed to the expected exponential increase in fuel viscosity with decreasing temperature. For all samples tested there is a drastic increase in pressure measured at the cloud point. When the fuel is at the cloud point and begins to precipitate waxes, these particles are relatively large and easily caught by the 4 μm filter. In our experiment there was no differentiation between fuel with and without CFI for the high efficiency media. In contrast, the ability of CFIs to modify the size and shape of wax crystals is observed for the 10

μm primary filter. On this less efficient filter, once the fuel is cooled to the cloud point the differential pressure immediately saturates the transducer at 50 PSI. Cold flow improver modified wax crystals are shown to be less problematic as they either pass through the filter or load with higher capacity.

At temperatures greater 5°F above the cloud point some experiments show additional pressure for additized fuel, as compared to the same experiment with unadditized fuel. We attribute pre-cloud point additional pressure to be from EVA that has precipitated from fuel to act as a nucleation point for waxes. The pre-cloud point additional pressure is observed for sample E with both media and sample A for only the $4\ \mu\text{m}$ secondary filter.

The amount of pre-cloud point pressure increase likely depends on the amount of EVA precipitated, the size of EVA particles, and both filter media efficiency and capacity. Though it is difficult to deconvolute all of these potential variables; the data presented in Fig. 4 hints that the precipitated EVA particles are in the size range of $1\text{-}10\ \mu\text{m}$. Further insight into the capture of pre-cloud point precipitated EVA particles is shown in Figure 5. In this experiment fuel was dosed with Sample E and filtered at 20°F with a variety of filter media. These media span a wide range of efficiencies and are from several manufacturers.

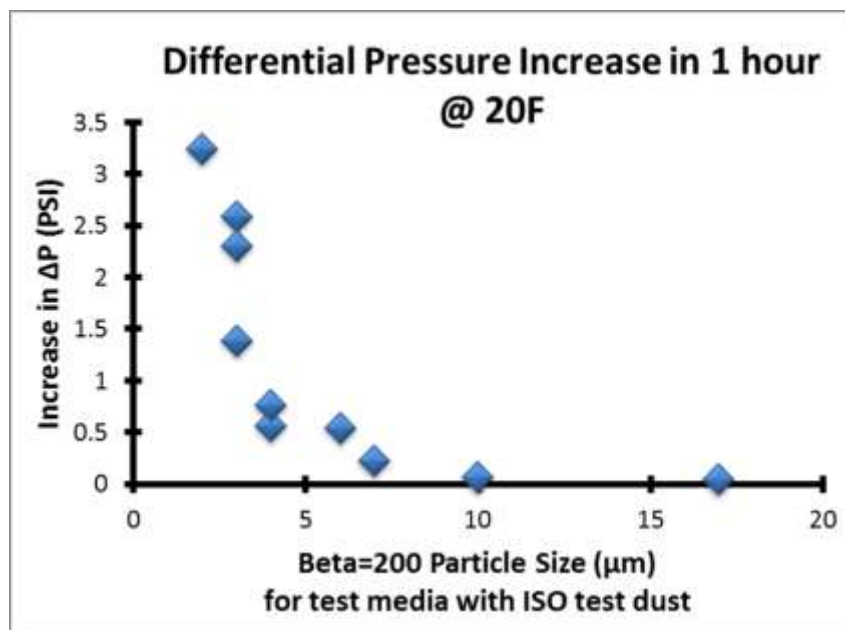


Figure 5. Differential pressure across filter media of varying efficiency as tested with Sample E CFI.

The ability of EVA based CFI to potentially plug a fuel filter was correlated versus the efficiency of the filter media. The horizontal axis of Fig. 5 is the rating of each filter media as measured by the particle size that gives 99.5% ($\beta=200$) removal efficiency per ISO 16889. This data shows a near step function change in differential pressure as the filter efficiency is increased to $3\text{-}4\ \mu\text{m}$. Again note that this is now the level of filtration required for protection of tier 3 and 4 high-pressure common rail fuel systems. Fortunately, similar to the dissolution of improperly

manufactured EVA, we find that application of heat is able to re-dissolve an EVA forced out of solution by cooling.

The thermal history of pre-cloud point precipitated EVA is shown in Figure 6. In this experiment a filter media with 99.5% removal efficiency of $\geq 3\mu\text{m}$ particles tested with additive sample E. Similar to previous experiments the fuel was quickly to 50°F and then cooled at 0.35°F/min. After the pressure from pre-cloud point precipitated EVA began to quickly rise, the fuel and experimental apparatus was warmed back to room temperature. We observe all pre-cloud point pressure from EVA precipitation to be thermally reversible. While there is significantly hysteresis in the process, the amount of hysteresis is likely dependent on the rate of heating.

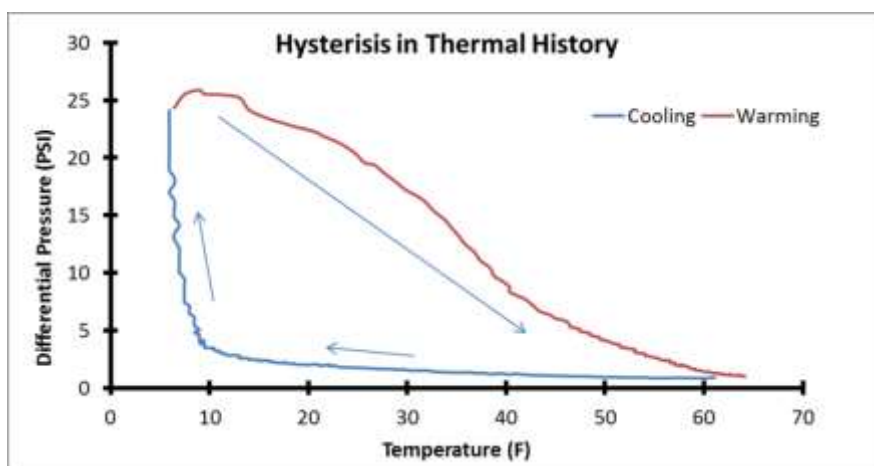


Figure 6. Hysteresis in thermal history of pre-cloud point precipitated EVA from additive sample E passed through a 3 μm filter.

The ability for pre-cloud point precipitated EVA to be forced back into solution at increased temperatures has tremendous implications. First consider the case of a bulk fuel filter exposed to constant cold temperatures during winter. In this application a filter that has prematurely plugged with precipitated EVA particles will likely remain plugged until warmer temperatures in spring. For a second perspective consider an on-engine fuel and filter system. In this case, if the engine can be cold-started, heat from recirculated fuel could potentially dissolve filter bound EVA back into fuel.

Conclusions

We have documented two possible problematic interactions of EVA based CFIs when used in combination with high efficiency fuel filtration. Precipitated EVA particles from either inadequate manufacturing practices or temperature dependent solubility have the potential to foul high efficiency filters. Since this level of filtration is now necessary for successful protection of high-pressure common rail fuel system, care must be taken to avoid potential premature plugging events.

References

1. ATC document 113 “Fuel Additives: Use and Benefits” Found online at <http://www.atc-europe.org/public/Doc113%202013-11-20.pdf>

Keywords Filtration, ULSD, Fuel Additive, Cold Flow Improver