

**A FUEL STABILITY STUDY
FILTERABLE AND ADHERENT INSOLUBLES AS FUNCTIONS OF TIME**

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INTRODUCTION

It is generally accepted that the insoluble substances that form in middle distillate fuels in storage are the result of an oxidative coupling of reactive molecules which may be of the same or of different species. It is also generally accepted that the reactive species are to be found among those containing a heteroatom such as nitrogen, sulfur, or oxygen and among unsaturated hydrocarbons. However, the number of reactive compounds is large and the chemical mechanism by which they are converted into insoluble products has not been established despite years of study.

In 1958, Sauer and coworkers⁽¹⁾ postulated the formation of hydroperoxides which then split out water to form aldehydes. The aldehydes then reacted with other peroxides to form peroxyhemiacetals which, in turn, decomposed to form monomeric oxidation products and condensed, esterified products of higher molecular weight. Another hypothesis noted by Taylor and Frankenfeld⁽²⁾ and by Por⁽³⁾ is based on a free radical chain mechanism.

From a study of U.K. stocks, Pedley and Hiley⁽⁴⁾ have suggested that phenalenes and indoles are the precursors of some fuel sediments. The phenalenes are known to oxidize to form phenalenones which can react by acid catalyzed condensation with indoles to form indolylphenalenes. These then form insoluble products by reaction with acids.

Pedley et al⁽⁵⁾ investigated Australian stocks and found that all fuels which proved to be unstable during storage contained both alkylindole and phenalene species. Marshman⁽⁶⁾ from a study of research blends made from fresh components obtained from U.K. and European refineries concluded that the stability of a fuel is related to the concentrations of phenalenes and indoles, but the relationship is not straightforward.

ACCELERATED TESTS OF STORAGE STABILITY

Such studies are useful in providing an understanding of the complex chemical mechanism by which sediment is formed. However, the person storing middle distillate fuels is more interested in the rate at which sediments will form. For example, the military and the Strategic Petroleum Reserve, both of which have to store large quantities of fuel, cannot tolerate unstable fuels.

For that reason, a number of test methods have been developed and standardized to provide an indication of the stability of a fuel. ASTM Test Methods D 2274, the accelerated stability procedure, and D5304, oxygen overpressure procedure, are two of the methods. The former has long been a required test in the Navy's distillate fuel specification; the latter is being considered as an alternate or replacement.

In Test Method D2274, which was used in obtaining the data to be presented in this paper, a 350 mL volume of filtered fuel is aged at 95°C for 16 hours while oxygen is bubbled through the fuel at 3 L/h. The fuel is then cooled and insolubles are recovered. Particulates (FI) are recovered by filtration and gums adhering (AI) to the glassware are recovered by solvent washing. The insolubles are weighed and their sum is reported in mg/100 mL as a measure of the fuel's oxidative storage stability.

PROCESS ANALYSIS

The reactions which lead to insolubles formation start as soon as the middle distillate fuel is produced and comes in contact with an oxygen-containing atmosphere. The rate of reaction depends upon the specific fuel system and the materials with which it comes into contact. Copper and some other metals are oxidation catalysts. Rust also has some catalytic properties. Acidic materials can catalyze some of the potential reactions. Consequently, some of the instability reactions may have already occurred prior to laboratory testing of a fuel sample. An early step in the Test Method D2274 procedure is the filtering of the fuel sample to remove any solids that may have formed or that may have entered from other sources.

Let us examine what we think occurs during a D2274 type of testing. First of all, some of the reaction products is bound to be soluble in the fuel, so it is only after the saturation limit is reached that particulates begin to appear in the fuel as filterable insolubles .

Second, during the period required to reach saturation, another rate process is already removing instability products from the fuel. It is an adsorption process, and Fick's law of diffusion defines the rate of diffusion of the instability products to the glassware surface:

$$Q = D(A)(c/t) \quad (1)$$

Q is the quantity diffusing to the adsorption surface per unit time, D is the diffusion coefficient, A is the area of the glassware wetted by fuel, and c/t is the concentration gradient between the bulk fuel and the surface of the glassware. Thus, while the instability reactions are placing reaction products in solution, the diffusion and adsorption process is removing material from solution and depositing it on the glassware.

Presuming that the reaction process is faster than the rate at which reaction products are removed as adherent insolubles, the solubility limits of the reaction products in the fuel will eventually be reached and the filterable insolubles will begin to precipitate from solution. As long as reaction products are produced at a rate faster than they can be removed by adsorption, excess material will precipitate to add to the quantity of filterable insolubles.

If the concentrations of the reactants is rate controlling, there will be a gradual decrease in the rate of formation of filterable insolubles. However, if reactant concentrations are high, other rate processes may be limiting. For example, the rate at which dissolved oxygen can be replenished from the oxygen which is bubbled through the fuel in Test Method D2274 may be the controlling process. In such cases, the rate of formation of FI would be constant, and a plot of cumulative FI as a function of stress time would be linear, until the concentrations of the reactive fuel components decreases to the point where their concentrations are controlling the rate.

Because the instability reaction products (IRP) in solution will remain constant at the saturation concentration, the rate of formation of adherent insolubles will be constant, i.e. a plot of cumulative AI versus time will be linear. However, once the formation of reaction products drops below the rate just sufficient to maintain saturation, the rate of adherent insolubles formation will begin to decrease, i.e. the slope will decrease and the cumulative AI will approach an asymptotic value.

If both the filterable insolubles and the adherent insolubles approach asymptotic values, the ratio of the two must also approach an asymptotic value.

EXPERIMENTAL PROCEDURE AND RESULTS

The author has previously reported some results obtained when twenty-one fuel stocks were individually stressed in a D2274 procedure using a range of stress times.⁽⁷⁾ The time response curves of total insolubles vs. stress time have an S-shape if the period is sufficiently long and the total insolubles level approaches an asymptotic value. The study showed that tests using a single stress time are incapable of fully defining the stability characteristics of a fuel. It was also found that pre-aging a fuel prior to determining its time response curve appeared to affect only the duration of the induction period.

The same twenty-one stocks and the same tests form the basis of this paper, in which we examine the manner in which stress time affects the individual components of total insolubles, i.e. the filterable insolubles (FI) and the adherent insolubles (AI). Properties of the stocks were presented in the earlier paper.

The experimental data tend to support the postulated mechanism. Figures 1 to 4 show the filterable insolubles, the adherent insolubles, and the ratio of filterables to adherents as functions of the time the four fuels were left in the 95°C bath. These illustrations were selected as representative of the twenty one stocks mentioned earlier. Similar curves were obtained with the other fuels.

Although fuels which had data points at five or more times and which had one or more data points representing times of sixty or more hours were preferred, the need to show representative fuels did not always permit such preferences to be honored. In general, the shapes of the curves were not as certain with fewer points or with a smaller range of times.

Figure 1 shows the time response curves for a light cycle oil (LCO). Note the initial linear responses of both the AI and the FI. A rate limiting phenomenon controlling the formation of filterable insolubles below 40 hours of stress is postulated. Above the 40 hour stress point, it appears the concentration of the active components of the fuel are controlling. The AI also exhibit a linear rate response below the 40 hour point, which is consistent with the postulated mechanism. The ratio of FI to AI seems to be approaching an asymptotic value of about 2.

Figure 2 shows the time response curves for a 40/60 volume percent blend of an LCO in a straight run (SR) fraction. The range of times ran only to 46.2 hours but, within that time range, we did obtain six data points. The curves indicate that saturation is not reached until 20 hours have elapsed. The standard 16-hour test would have shown this to be a very stable fuel with very low insolubles whereas, in another 20 hours, it approached its asymptotic level of roughly 3.5 mg/100 mL.

The FI curve shows that the concentrations of active components is controlling, and the AI curve supports the adsorption hypothesis because it is linear. The FI/AI ratio curve seems to be reaching an asymptotic value of about 2.

Figure 3 shows the time response curves for a 30/70 blend of an LCO with an SR fraction. The FI time response curve shows a decreasing rate of FI formation, so the concentrations of active ingredients is postulated as controlling. The AI response curve is again linear, and the ratio curve seems to be approaching an asymptotic value of about 1.

Figure 4 shows the time response curve for a blend of a high sulfur heavy diesel fuel in a CAT 1H fuel. The maximum stress time is 40 hours, but we do have five data points. Linear fits are obtained for both the FI and the AI, and the ratio of the two seems to be reaching an asymptotic value of about 3.5.

FINDINGS AND CONCLUSIONS

1. Formation of FI remains essentially zero until the fuel is saturated with instability reaction products (IRP's). Thereafter, the rate of FI formation may be linear if there is a limiting rate factor such as oxygen supply, or it may decrease as reactive components are depleted.

2. Once a fuel is saturated with IRP's, AI formation is constant until reaction rates are too slow to keep the fuel saturated.

3. After the fuel becomes saturated with IRP's, the FI/AI ratio starts to approach a constant value. Experience indicates this is often about 1 or 2. We have seen no value above 6.

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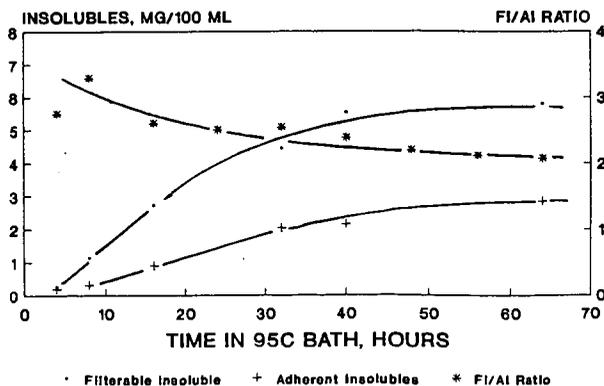


Fig. 1 - Time response curves for a light cycle oil, showing FI, AI, and the FI/AI ratio as functions of time.

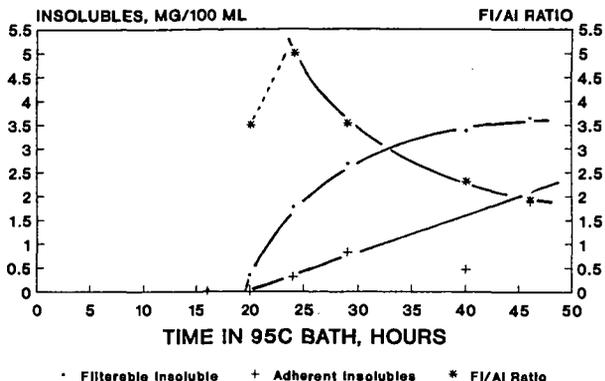


Fig. 2 - Time response curves for a 40/60 volumetric blend of LCO in an SR stock, showing the FI, AI, and FI/AI ratio as functions of stress time.

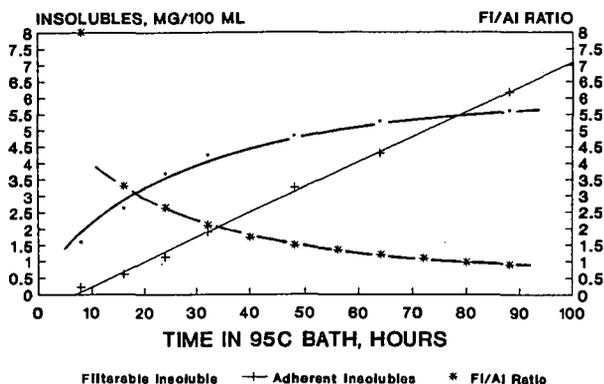


Fig. 3 - Time response curves for a 30/70 blend of a blend of an LCO in an SR stock, showing the FI, AI, and FI/AI ratio as functions of stress time.

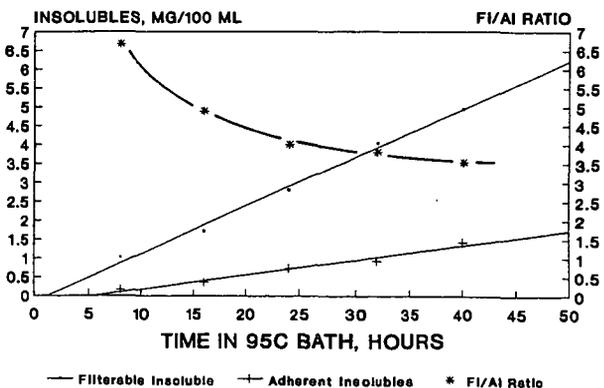


Fig. 4 - Time response curves for a blend of high sulfur, heavy diesel fuel in a CAT 1H fuel, showing the FI, AI, and FI/AI ratio as functions of time.