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A FUEL STABILITY STUDY: TOTAL INSOLUBLES AS A FUNCTION OF TIME

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INTRODUCTION

The David Taylor Research Center, in cooperation with the Naval Research Laboratory (NRL) plus contract laboratories, has been studying the effectiveness of stability additives in Naval Distillate fuels since 1983. Initial studies of the antioxidants permitted in Naval Distillate showed that not all the antioxidants are equally effective and that some might even be detrimental.⁽¹⁾ Later work with nine commercial additives in a number of fuel stocks showed that two of the additives were consistently more effective than any of the other seven additives.⁽²⁾

The first test of commercial additives was run on a fuel stock containing 40% light cycle oil. When a low level of insolubles (about 0.6 mg/100 mL of fuel) was obtained, it was considered too low to obtain a good evaluation of the effectiveness of additives. We therefore investigated the effect of stress times greater than the 16 hours prescribed in the ASTM D2274 procedure. Subsequently, we conducted such time studies on a total of 21 fuel stocks. This paper summarizes the results of those studies and discusses the implications of our findings.

MATERIALS AND PROCEDURES

Materials - The 21 fuel stocks used in the study included one straight run (SR) stock, 4 light cycle oils (LCO), 10 SR/LCO blends containing 30% (vol) LCO, 3 containing 40%, 2 containing 15%, and a blend of high sulfur, heavy diesel fuel in a CAT 1H fuel. The stocks were obtained by NIPER (National Institute for Petroleum and Energy Research) from Gulf coast, west coast, east coast, and mid-continent refineries. Table 1 shows available ranges of properties measured on the stocks (not all stocks).

Procedures - The ASTM D2274 test for the oxidation stability of distillate fuel by the accelerated method was used, with modifications.⁽³⁾ The primary modification was the use of residence times both less than and greater than the 16 hours at 95°C specified by the test method. The maximum time used was 96 hours. In a second modification, we cleaned the apparatus without using chromic acid solution. In a third modification, we evaporated adherent gum solvent by other than the jet gum procedure.

RESULTS AND DISCUSSION

The 21 time response curves of total insolubles as a function of residence, or stress time, are shown in Figures 1 through 5. They exhibit a tendency toward an S-shaped curve consisting of an induction period, followed by a period of rapid formation of total insolubles, and finally a leveling off to some final value. The curve obtained with Fuel 30-10 (Figure 2) is the best example of this tendency. Sauer and coworkers⁽⁴⁾, using a somewhat different test procedure, published similar curves as long ago as 1958. Cooney and coworkers⁽⁵⁾, Hazlett and coworkers⁽¹⁾, and Westbrook and coworkers⁽⁶⁾ also obtained similar curves in 80°C bottle tests.

Various mechanisms have been proposed for the formation of insolubles in fuels. Sauer and coworkers⁽⁴⁾ suggested the side-chain oxidation of reactive compounds in a fuel to form hydroperoxides which then decomposed to form aldehydes; the aldehydes were postulated to react with other peroxides to form peroxyhemiacetals, which in turn decomposed to form condensed, esterified higher molecular weight products. They suggested a typical sediment molecule containing a pyrrolic structure.

Frankenfeld and coworkers⁽⁷⁾, from a study of dimethylpyrrole (DMP) in jet fuel, concluded that sedimentation appeared to be a free radical, autoxidative reaction involving a mechanism similar to that proposed by Sauer. They also concluded from a study of shale liquids that nitrogenous sediment formation in such liquids involves oxidative oligomerization of nitrogen compounds and that the neutral, heterocyclic compounds such as alkyl pyrroles and indoles appear to be especially reactive.

Hazlett and coworkers⁽⁸⁾ in a study of diesel fuels doped with DMP and stressed at 80°C, conducted elemental analyses, gas chromatographic analyses, and infrared spectroscopic examinations of the sediment. They remarked on the consistency of the elemental analyses on sediments from tests conducted under a wide variety of conditions. They found the atomic ratio of carbon to nitrogen was about 6:1 indicating the sediment was derived from the DMP.

The shape of the curves found in the current study is consistent with such past work. An induction period is consistent with the theory of consecutive reactions and the approach to a final value of total insolubles is consistent with the findings of an oligomerization with a specific chemical composition. We suggest that a few reactive species present in a fuel, primarily the reactive nitrogen compounds identified by Frankenfeld are involved in sediment formation. The rate at which such formation takes place, however, may be a function of the acidity and solvency of the system, of the presence of catalytic substances such as copper compounds, and of the presence of inhibitors, either naturally present or added.

Figures 1 - 5 also show the normal 16 hours of residence is frequently too early to catch the part of the curve where total insolubles increase at a fast rate. In most cases, the breakpoint has occurred by 20-24 hours. See, for example, the curves for Fuel 30-10 in Figure 2 and for LC-2 in Figure 3. The total insolubles produced in LC-2 by the end of 32 hours of residence time is 20-times the total insolubles produced in 16 hours.

Thus, the curves make us realize that no single-time test of short duration can be adequate for defining the behavior of a fuel in ambient storage. Rather, we need a test method that determines the induction period (the breakpoint time), the rate of increase of insolubles formation following the breakpoint, and the ultimate total insolubles formed after a long period of oxidative stability testing.

As a by-product of our time response program, we obtained some interesting data on the effect of light cycle oils (LCO) on the stability of straight run stocks. In two cases, we had available both the straight run stock and the LCO in addition to blends of 15%, 30%, and 40% LCO in the straight run. In the one case, we ran time response curves for the entire gamut of concentrations. The total insolubles obtained after 16 hours, 32 hours, and 40 hours of residence time are shown in Figure 6 as a function of the LCO concentration.

The lack of linearity of the curves in Figure 6 indicate that total insolubles obtained with the straight run stock and with the LCO are not additive. Addition of the more stable straight run stock to LCO does not provide a simple diluent effect. The chemistry responsible for this effect is not known, but it may be related to the acidity of the system, which some investigators, such as Hazlett⁽⁹⁾, postulate as having a catalytic effect on the reactions involved in insolubles formation.

We have one additional figure, a figure which shows the effect of pre-aging. Pre-aging was accomplished by sparging a fuel with air and then allowing the sample to sit for a month at ambient laboratory temperatures before running D2274-type tests. Figure 7 compares the time responses of the pre-aged fuel and of the same fuel prior to pre-aging. The pre-aged fuel started rapid formation of insolubles at a much earlier point in time than the unaged fuel. Beyond the point at which 1.5 mg of total insolubles per 100 mL of fuel have been formed, the two curves are essentially parallel. This indicates the rate of formation of new insolubles is the same for the pre-aged and unaged fuel.

We postulate that the pre-aging permitted the formation of intermediates which would normally be produced during the early stages of the D2274 test. Then, when the pre-aged fuel was tested by the D2274 procedure, the formation of the insolubles could start immediately. We further postulate that, once the intermediates have been formed, the further reaction to form total insolubles is the same in the two cases.

FINDINGS AND CONCLUSIONS

1. Time response curves of total insolubles vs. residence time have an S-shape if carried for a sufficient period, and the total insolubles level approaches an asymptotic value.

2. Single time stability tests are incapable of fully defining the stability characteristics of a fuel.

3. The blending of two fuel stocks may not result in sediment formation that is a linear function of the sediments produced by each fuel stock alone.

4. Pre-aging a fuel stock prior to determining its time response curve affected only the length of the induction period.

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TABLE 1
RANGES OF PROPERTIES OF STOCKS USED IN TIME STUDY

Property	30% Blends	40% Blends	LC Oils	Other Stocks
Density, kg/m ³	840 - 895	859 - 901	896 - 953	836 - 869
Viscosity, cSt	2.0 - 3.8	2.6 - 3.2	2.6 - 3.3	2.9 - 3.2
Distillation, °C				
IBP	144 - 223	180 - 221	213 - 224	198 - 217
10% Point	207 - 258	234 - 244	243 - 254	232 - 243
50% Point	232 - 292	270 - 283	269 - 283	267 - 283
90% Point	290 - 332	313 - 335	306 - 326	319 - 335
End Point	324 - 349	345 - 349	323 - 329	338 - 349
Cetane Index	38 - 49	36 - 48	23 - 37	44 - 54
Sulfur, %	0.2 - 0.8	0.2 - 0.9	0.3 - 1.0	0.3 - 0.6
Nitrogen, mg/L	43 - 266	44 - 246	61 - 428	25 - 151
TAN, mg KOH/g	.02 - .23	.02 - .15	.02 - .06	.04 - 0.25
Bromine No.	.23 - .43	.51 - 1.13	0.47	.12 - .47

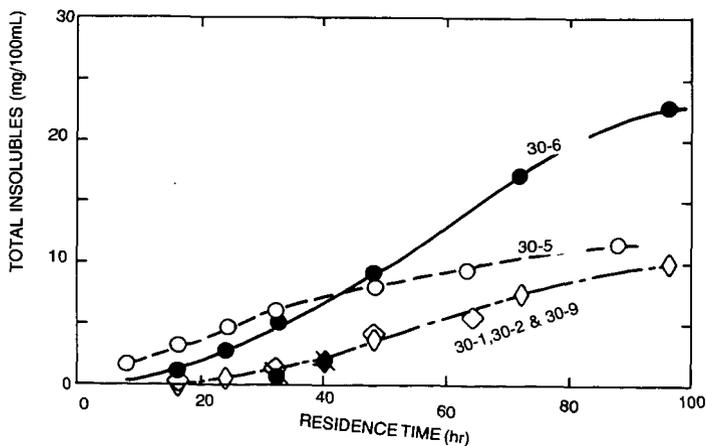


Fig. 1 - Time response curves for five fuels containing 30% LCO and 70% SR (Fuels 30-1, 30-2, 30-5, 30-6, and 30-9).

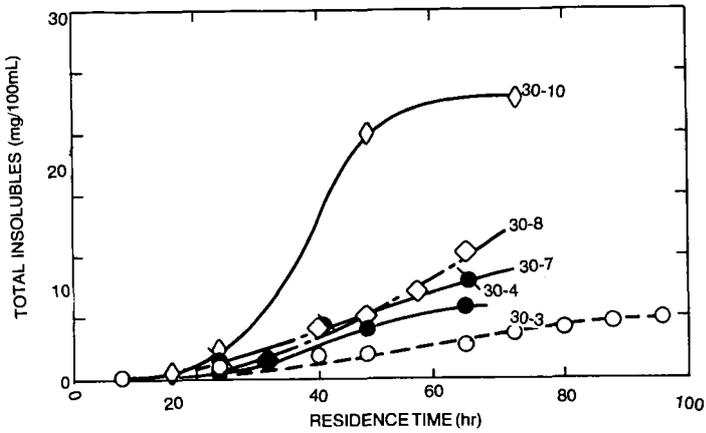


Fig. 2 - Time response curves for five fuels containing 30% LCO and 70% SR (Fuels 30-3, 30-4, 30-7, 30-8, and 30-10)

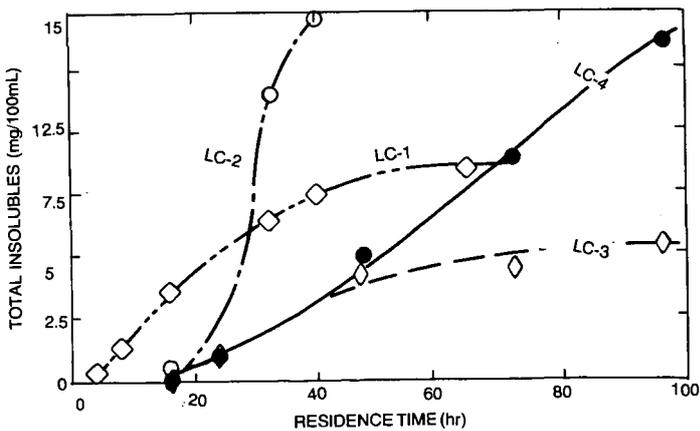


Fig. 3 - Time response curves for four light cycle oils

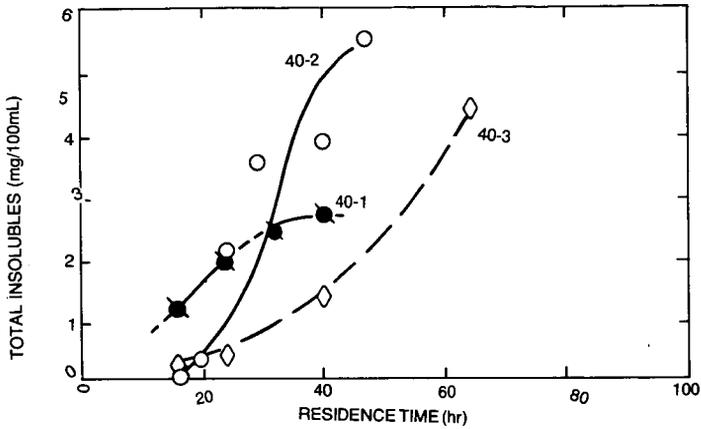


Fig 4 - Time response curves for three fuels containing 40% LCO and 60% SR.

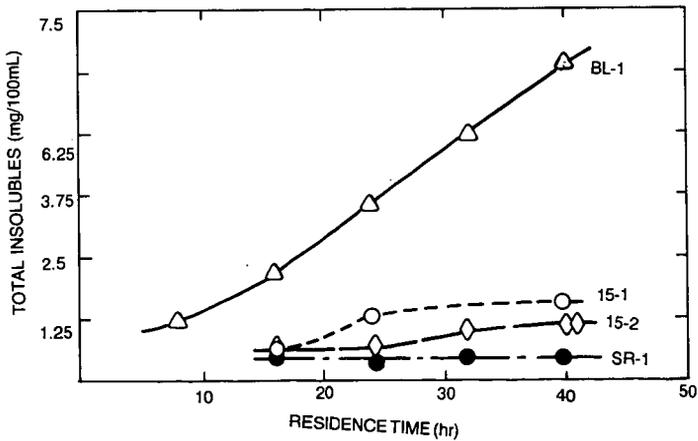


Fig 5 - Time response curves for four miscellaneous fuels (Fuels 15-1 and 15-2 containing 15% LCO; straight run Fuel SR-1; and Fuel Blend BL-1, a high sulfur diesel fuel in CAT 1H fuel).

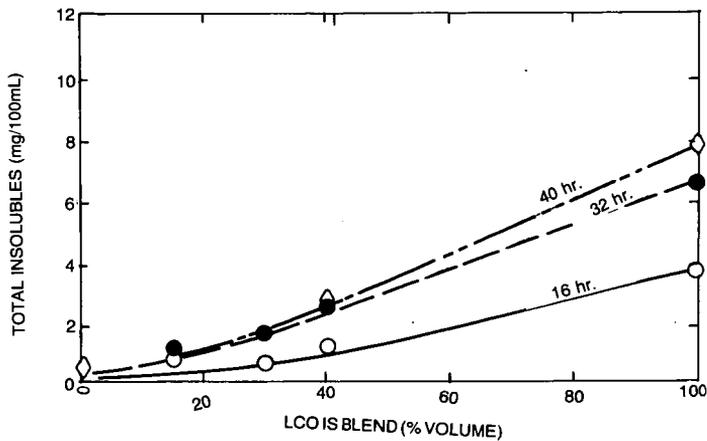


Fig. 6 - Curves showing effect of LCO concentration in straight run/light cycle oil blends on the total insolubles formed in 16 hours, in 32 hours, and in 40 hours of D2274-type stressing.

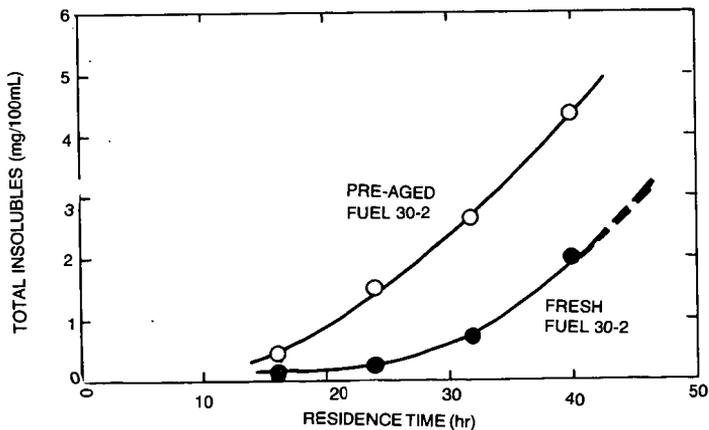


Fig. 7 - Time response curves for pre-aged and unaged Fuel 30-2; the effect of pre-aging on the formation of total insolubles.