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FUEL STABILITY FOAM

A.J. Power, W. Arfelli and R.K. Solly

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FUEL STABILITY FOAM

A.J. Power, W. Arfelli and R.K. Solly

ABSTRACT

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A new means of increasing the chemical stability of petroleum fuel during storage has been developed. Distillate fuel blends have been shown to form significantly less total particulate matter (comprising the sum of the suspended insoluble and adhered particulate matter) following storage in contact with Fuel Stability Foam (FSF) than similar reference fuels aged in the absence of FSF. The most effective FSF material has been found to be a reticulated polyurethane which maximizes the fuel stabilizing properties. This effect is at least equivalent to that of any known fuel-soluble chemical stabilization additive. Enhanced filterability and decreased colouration of fuels after storage in contact with FSF were also observed. Total insolubles in aged fuels containing known deposit promoting agents, including carboxylic acids, soluble copper and aromatic thiols, were reduced to low levels by the presence of FSF. Contributing mechanisms for the stabilizing action of FSF include adsorption by the FSF of chemical precursors to the particulate matter, adsorption of soluble particulate matter, solution of solid particulate matter in the foam and adsorption and interaction with species to modify the acid/base environment of the fuel. The advantages of using FSF for fuel stabilization in both military and non-military fuel systems are considered.

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Page 1

CONTENTS

	Page No.
1. INTRODUCTION	1
2. EXPERIMENTAL	3
2.1 Fuel Characterization	3
2.2 Fuel Soluble Additives	3
2.3 Polyurethane (PU) Foams	3
2.4 Fuel Ageing in Absence of PU Foam	4
2.5 Measurement of Filtration Times and Total Insolubles	4
2.6 Fuel Ageing in Presence of PU Foam	5
2.7 Pretreatment of Fuel with PU Foam	5
2.8 Multiple Use of PU Foam Samples	5
2.9 Methylene Chloride Extract of Aged PU Foam	6
2.10 Instrumentation	6
3. FUEL STABILITY PARAMETERS	6
3.1 Total Insolubles	6
3.2 Filterability	7
4. RESULTS	8
4.1 Ageing at 43.3°C	8
4.2 Ageing at 80°C and 120°C	9
4.3 Comparison with Fuel Soluble Stability Additives	10
4.4 The Effect of Fuel Destabilizing Agents	10
4.4.1 Copper Naphthenate	10
4.4.2 Chloroacetic Acid	11
4.4.3 Benzenethiol	11
4.4.4 1-Hexadecanethiol	11
4.5 Pretreatment by Initial PU Foam Immersion	12
4.6 Repeated Ageing of PU Foams	12
4.7 Mass Variations of PU Samples	13
5. DISCUSSION	13
5.1 Formation of Total Insolubles	13
5.2 Effect of PU Foam Upon Total Insolubles	13
5.2.1 With Previously Degraded Fuels	14
5.2.2 With Carboxylic Acids	14
5.2.3 With Thiols	15
5.2.4 With Soluble Copper	15

Accession For		13
NTIS GRA&I	<input checked="" type="checkbox"/>	13
DTIC TAB	<input type="checkbox"/>	13
Unannounced	<input type="checkbox"/>	
Justification		14
By		14
Distribution/		15
Availability Codes		
Dist	Avail and/or Special	
A-1		

CONTENTS  
(continued)

	Page No.
<b>5.3</b> <i>Effect of PU Foam Upon the Filtration Index</i>	15
<b>5.4</b> <i>Mechanism of Fuel Stabilization by PU Foam</i>	16
<b>5.4.1</b> <i>Modification of Chemical Equilibria</i>	16
<b>5.4.2</b> <i>Deposition of Insolubles on PU Foams</i>	16
<b>5.4.3</b> <i>Acid Catalysis</i>	17
<b>5.4.4</b> <i>Comparison with Liquid Stability Additives</i>	17
<b>5.4.5</b> <i>Soluble Stability Agents from PU Foam</i>	18
<b>6.</b> CONCLUSIONS	18
<b>6.1</b> <i>Effectiveness of PU Foams as Fuel Stability Agents</i>	18
<b>6.2</b> <i>Use of PU Foams with Hydrocarbon Fuels</i>	19
<b>7.</b> REFERENCES	21
APPENDIX A <i>Fuel/PU Foam</i>	
APPENDIX B <i>Fuel/PU Foam/FOA Fuel Additives</i>	
APPENDIX C <i>Fuel Additives - Fuel Ageing: 65°C - 43 days</i>	
APPENDIX D <i>Fuel Additive - Fuel Ageing: 80°C - 13 days</i>	
APPENDIX E <i>Fuel/PU Foam Pretreatment</i>	
APPENDIX F <i>Multiple Use of PU Foam Samples</i>	
TABLE 1 <i>Fuel Properties</i>	
TABLE 2 <i>Classification of PU Foams used in Fuel Stabilization Experiments</i>	
TABLE 3 <i>Action of PU Foam on Degraded Fuel</i>	
FIGURE 1 <i>Arrhenius Plot of Particulate Formation</i>	
FIGURE 2 <i>Effect of PU Foam Type (Ageing 43C - 26 weeks)</i>	
FIGURE 3 <i>Effect of PU Foam Type (Ageing 80C - 7 days)</i>	
FIGURE 4 <i>Comparison of Liquid Additives with PU Foam (Ageing 80C - 13 days and 120C - 3 days)</i>	
FIGURE 5 <i>Effect of Copper Naphthenate (Ageing 80C - 13 days)</i>	
FIGURE 6 <i>Effect of Chloroacetic Acid (Ageing 65C - 43 days)</i>	
FIGURE 7 <i>Effect of Benzenethiol (Ageing 65C - 43 days)</i>	
FIGURE 8 <i>Effect of 1-Hexadecanethiol (Ageing 65C - 43 days)</i>	
FIGURE 9 <i>Infrared Spectrum of Methylene Chloride Extract from Aged FSF 13</i>	

## FUEL STABILITY FOAM

### 1. INTRODUCTION

Research on petroleum diesel distillate instability has been continuing for many years, and it is apparent from a review of the literature (to 1984) by Pedley [1], that the topic was actively pursued at a number of centres during the 1950's. This was followed by a period of relative inactivity in this field during the 1960's and 70's, presumably because abundant stocks of stable straight run distillate (SRD) were available. During the 1980's, there has been a resurgence of research in many areas of fuel instability science, culminating in the introduction of regular international conferences on many aspects of long-term storage of fuels [2]. The renewed interest in distillate fuel instability is related to market forces. Increasing amounts of catalytically cracked light cycle oil (LCO) are being blended into refinery SRD streams to increase the yield of middle distillates to meet higher consumer requirements. The LCO contains chemically unstable species which contribute significantly to fuel instability and insoluble particulate formation. The insoluble organic matter can plug fuel system filters and foul diesel injection nozzles.

For strategic reasons, military fuels are often stored for quite long periods, and it is during storage that undesirable fuel degradation products form. Subsequent use of degraded fuel can result in reduced operability or mechanical failure in Defence materiel. Therefore, storage stability of distillate fuels is a matter of increasing Defence concern, and Defence establishments worldwide are contributing to research in this field [2].

In order to supply a stable distillate fuel, there are three main procedures. The first is to restrict the fuel to refinery streams containing only stable SRD. Due to demand for distillate fuel, most refineries cannot produce sufficient automotive diesel fuel by restricting the output solely to SRD. The second means is to hydrotreat the LCO prior to its addition to the output stream. The hydrogenation process deactivates those species which contribute to fuel instability reactions. Most refineries in Australia hydrotreat LCO prior to its addition to automotive diesel fuel. The third method is to add liquid chemical stabilizing additives to fuel which is likely to form insoluble products from chemical degradation during storage.

The treatment choice depends on the storage stability of the fuel and several highly accelerated test methods have been developed to predict storage life. However, correlation of these tests with ambient storage conditions is poor [3,4]. Mild accelerated thermal ageing at temperatures in the region 43-80°C gives much better correlation with ambient storage [3], but the periods required for measurable fuel degradation are too long for such tests to have practical diagnostic significance for the refinery.

In the absence of a reliable, rapid predictive test, all fuel containing unhydrogenated LCO may be considered as unstable and should be treated. The adverse effects of LCO components on fuel stability are not usually diminished in proportion to dilution with relatively stable SRD [5,6] and some SRD fuels in fact cause significantly greater formation of insolubles, when blended with LCO, than the LCO does alone [7]. The chemical processes responsible for this effect have not been identified, and therefore the influence of SRD components on the stability of fuel blends is unpredictable.

The performance of commercially available fuel soluble chemical stability additives has recently been evaluated at this Laboratory [5,8]. Stability properties were measured with respect to deposit formation and fuel filterability. Tertiary alkylamine additives have been shown to be much more effective than free radical inhibiting antioxidants for suppressing deposit formation [9], and the performance of one such amine, Du Pont Fuel Oil Additive No. 3 (FOA#3) [10] (containing *N,N*-dimethylcyclohexylamine [11]), was studied in detail. Evidence was obtained to indicate that diesel distillates degrade to produce deposits predominantly by an acid catalysis mechanism, rather than by free radical chemistry [5]. The strong deposit-forming influence of some organic acids, added at various concentrations to blends of SRD and LCO, was counteracted stoichiometrically by the amine, which was therefore considered to act by modifying the acid/base chemistry of the fuel. Hindered phenols and phenylenediamine, which reduce the rate of free radical oxidation processes, were ineffective in reducing deposit formation in automotive diesel fuel [9].

In a related study [8], it was demonstrated that addition to fuel blends of FOA#3, as well as other stabilizing additives, and a dispersant, did not significantly decrease filtration times of aged fuel compared to the fuel without additive. The dispersant increased filtration times, and there was generally poor correlation between the amount of suspended fuel particulate matter and fuel filterability. It was concluded that fuel stability tests based solely on the amount of particulate matter were unlikely to be fully indicative of filterability problems, and that a filterability test is the most appropriate for evaluating problems which arise from use of aged distillates.

The concentration of the tertiary alkylamine in FOA#3 has been found to decrease during fuel storage [5]. In stored fuel the level of this substance could drop to the point where it becomes ineffective in inhibiting fuel degradation. This potential source of uncertainty in the use of tertiary alkylamines is common to all soluble fuel additives used for a wide range of functions by the oil industry. Addition of fuel stabilizing agents is largely at the discretion of the refinery, or bulk fuel distributor in the market chain. Therefore, consumers of distillate fuel are generally unaware of factors which could affect the storage stability of a fuel consignment. Military fuels are frequently supplied to specifications, but this offers no indemnity against degradation of distillate fuels during storage. Soluble additives are consumed with the fuel in the engine combustion chamber and further additions of stabilizer are required for each new batch of fuel. Materials which have chemical stabilizing capabilities similar to the amines used as stability agents, but which could remain indefinitely in the fuel tank, offer the potential to stabilize each batch of fuel as it is added to the tank.

Polyurethane (PU) foams contain polar groups which include carbamate, amide, urea, biuret, isocyanurate and allophanate which may interact with the polar species responsible for deposit formation. PU foams have been reported to have the capability of absorbing phenols and polar compounds from liquid hydrocarbons [12,13]. Removal of phenols and other polar acidic species would modify the acidity of fuel. Phenolic compounds have been found to participate in fuel degradation mechanisms via phenolic oxidative coupling [14,15]. They are usually present in significant concentrations in petroleum middle distillate fractions, and their removal by caustic extraction or hydrotreatment reduces the formation of particulate matter in the fuel. Removal of the phenols by adsorption on to PU foams should increase storage stability.

PU foams possess properties which make them applicable for use in fuel systems. They do not suffer significant structural damage when immersed in hydrocarbon liquids. Some swelling may occur with foams in liquids containing high levels of aromatic compounds, but this effect is reversible when the foams are removed from the liquid. Some reticulated foams are manufactured specifically for immersion in hydrocarbon fuels for slosh attenuation. They are also claimed to provide explosion suppression by minimizing propagation of explosive air/fuel mixtures during fuel tank rupture [16]. Foams containing either polyether or polyester polyols are fuel-compatible, but the polyether variety is considerably less susceptible to hydrolysis. In this report, the fuel stabilizing properties of a number of PU foams are investigated.

## 2. EXPERIMENTAL

### **2.1 Fuel Characterization**

The test fuel was a 30% blend of a thermally cracked LCO with SRD. The latter fuel was that designated as "ADO" in previous studies [5]. The LCO component, which has also been described elsewhere [8], was maintained at  $-20^{\circ}\text{C}$ , except when being sampled. Properties of the fuels are listed in Table 1. All fuel blends were filtered through  $0.8\ \mu\text{m}$  absolute membranes immediately prior to use.

### **2.2 Fuel Soluble Additives**

Benzenethiol, chloroacetic acid, copper naphthenate and 1-hexadecanethiol were from commercial laboratory suppliers and the FOA#3 and FOA#15 fuel additives were from du Pont. All were dissolved in toluene at a concentration 100 times that required for fuel ageing studies. The chemicals were added to the fuel blend just prior to commencement of an experiment.

### **2.3 Polyurethane (PU) Foams**

PU foam samples used in the experiments described below were obtained from commercial manufacturers. General details of the foams are given in Table 2. Foams containing polyether and polyester polyols, either with reticulated or non-

reticulated structures were used to investigate the relationship between the chemical and physical form of the foams and their performance as fuel stabilizing additives. Air flow ( $\text{m}^3/\text{h}$ ) measurements were available for some foam samples (Table 2). Reticulated foams #2, 5, 10-13, for which these data were unavailable, should have similar air flow to the other reticulated foams #3, 4 and 9. Foam #1 would probably have had an air flow similar to other non-reticulated foams (Table 2;  $< 10 \text{ m}^3/\text{h}$ ). Air flow measurements were useful as a qualitative guide for assessing flow of fuel through foam samples in fuel stability trials.

## 2.4 Fuel Ageing in Absence of PU Foam

Experiments were conducted in 300 mL borosilicate Erlenmeyer flasks equipped with plastic screw caps and Teflon liners which were loosely screwed so the flasks were not totally sealed. No loss of liquid was observed in any experiment. Glassware was cleaned by washing sequentially with gum solvent (1:1:1 acetone, methanol and toluene), ethanol and water, then soaked overnight in mildly alkaline low sudsing detergent, rinsed in hot water, and dried at  $110^\circ\text{C}$  in an air oven (75 min). Final conditioning was as described in Section 2.5.

Rapid accelerated ageing of fuel samples (130 ml) was carried out in a forced fan oven maintained at  $65^\circ$ ,  $80^\circ$  and  $120^\circ\text{C}$  ( $\pm 0.5^\circ\text{C}$ ) for periods from 3-43 days. Mild accelerated ageing was carried out in an oil jacketed oven at  $43.3 \pm 1^\circ\text{C}$  for 26 weeks. After ageing was complete, duplicate samples were removed and allowed to cool in the dark (16 h). Immediately prior to the filtration and total insolubles measurement, the samples were vigorously swirled (1 min) and then allowed to stand (1 min). All of the aged fuel in the flask was added to the constant pressure filtration apparatus as described below. Following filtration measurement, the flasks were washed with pre-filtered light petroleum ether (b.p.  $50-70^\circ\text{C}$ ;  $3 \times 50 \text{ mL}$ ), each washing being filtered through Whatman (No. 540) cellulose fibre membranes with nominal pore size of  $8.0 \mu\text{m}$ . In fuel ageing trials, duplicate samples of the respective fuel blends without additives were carried through all procedures for comparison with duplicate sample blends containing additives.

## 2.5 Measurement of Filtration Times and Total Insolubles

Filtration measurements were carried out in a stainless steel pressure bomb (145 mm high, 45 mm diameter). A stainless steel membrane holder was attached to the base of the bomb by a 5 mm internal diameter connector which could be disassembled into two sections by a screwed collar. The membranes (Whatman No. 540) were supported on a 25 mm stainless steel mesh disc clamped by the screwed collar between a Teflon 'O' ring at the base and a Viton 'O' ring on top. After assembly, the filtration diameter of the membrane was 23 mm. The experiment was commenced by assembling dual 25 mm diameter filtration membranes (pre-washed with light petroleum and air dried) in the holder. The aged fuel was added to the bomb, the detachable screw top screwed on to the bomb and a valve at the top was operated to pressurize the bomb with nitrogen to 29 kPa (4.2 p.s.i.), maintained by means of a mercury or water manostat. The temperature of the fuel was kept constant at  $25 \pm 1^\circ\text{C}$  during filtration. The time for filtration of 100 mL of fuel was recorded. After filtration of an aged fuel, the bomb and membranes were washed with light petroleum ( $3 \times 50 \text{ ml}$ ) and the washings were also pressure filtered through the membranes.

The separated membranes and the flasks were dried under vacuum at 110°C (1 h). Vacuum was maintained in the oven while it cooled overnight to minimize oxidation of the organic particulate. Flasks and membranes were removed and equilibrated at ambient temperature for at least 1 hour before weighing. The amount of particulate was obtained from the difference in the mass between the top and the bottom membranes before and after the filtration. Similarly, the mass of adhered gum was recorded and corrected for the average of the difference in the mass of two blank flasks carried through all procedures without fuel.

## **2.6 Fuel Ageing in Presence of PU Foam**

The above procedures were repeated in experiments with PU foam additives. Additional procedures relating to handling of the foams in these experiments were as follows. Pieces of foam (40 x 30 x 10 mm), suitable for complete immersion in 130 mL fuel samples, were used. A procedure for weighing foam samples prior, and subsequent, to fuel ageing experiments was developed. The samples were swirled in a flask with filtered light petroleum (3 x 50 mL), and dried successively in air at ambient temperature (0.5 h), forced-air oven at 50°C (1 h), under vacuum at room temperature (3 h), and equilibrated at ambient temperature for at least one hour before weighing.

Fuel blends were prepared immediately before use and measured amounts of the toluene concentrate of fuel soluble additives were then mixed with the experimental aliquots. The foam was tamped with a flat-ended glass rod to remove entrained air for complete permeation of the foam with fuel. This process was much easier for the reticulated than the non-reticulated foams. Work-up for measurement of filtration times and total insolubles was conducted as described previously, but with the foam sample removed from the flask. The foam samples were weighed after the standardized weighing procedure. The light petroleum washings from the foam were passed through the filtration bomb membrane following fuel filterability measurement to collect loosely attached particulate dislodged from the foam.

## **2.7 Pretreatment of Fuel with PU Foam**

Samples of foam #1, which had been immersed in the fuel blend samples in the dark for five days at ambient temperature, were withdrawn from fuel contact. One of these fuel samples was set aside briefly, while two others were treated with fresh foam samples at 120°C for 3 and 7 hours, respectively. After cooling, and withdrawal of the latter foam samples from the fuel, all of the treated fuel samples were aged at 80°C for 14 days in the absence of foam, along with the untreated reference fuel.

## **2.8 Multiple Use of PU Foam Samples**

Samples of foams #1 and #2 were aged with fuel samples (130 ml) for 3 days at 120°C. Following standard work-up, the same foam samples were again aged with fresh fuel aliquots under the same conditions. The foams were not cleaned with solvents or treated with other chemicals between runs. The above experiment was repeated a third time, with the ageing period extended to 4 days.

## 2.9 Methylene Chloride Extract of Aged PU Foam

Following ageing with fuel and work-up, sample foam #13 (Table 2) from the 43.3°C/26 week test was extracted with methylene chloride (40 ml). The solvent was concentrated under reduced pressure (30°C) to about 3 ml, for instrumental analysis of extractable material. Subsequent removal of the solvent yielded a viscous brown oil (8 mg). A fresh sample of the same foam yielded no extractable material.

## 2.10 Instrumentation

Gas chromatography (GC) of the methylene chloride extract above was run using a Varian 3700 gas chromatograph with FID on a 25 m x 0.33 mm i.d. fused silica column (SGE - BP 1 - 0.5), with temperature programming from 30 - 250°C at 4°C min<sup>-1</sup>. Gas chromatography/mass spectrometry (GCMS) analysis of the extract was carried out on a VG 7035 mass spectrometer equipped with a fully laminated magnet and a model 3 Digital scanner. A Varian model 3700 GC was interfaced, and the fused silica column terminated directly in the ion source. Infrared spectra were recorded on a Perkin-Elmer 580B spectrometer and the data were processed on a Perkin-Elmer model 3600 data station. Samples were prepared as films of the evaporated methylene chloride extracts, deposited from chloroform solution on KBr windows.

## 3. FUEL STABILITY PARAMETERS

### 3.1 Total Insolubles

Total insolubles, considered to be the most meaningful measurement of fuel degradation [5], are determined as the sum of suspended particulate matter and material adhered to the walls of the container (adhered particulate). The variation in amount of total insolubles as a function of the temperature and time of fuel ageing has been considered by Cooney, Beal and Hazlett [17]. In a plot of time on a logarithmic scale versus temperature in degrees Celsius for 17 experiments yielding equivalent total insolubles, a straight line could be drawn through results for experiments at 43.3°C, 80°C and 150°C. Extrapolation of this line to a time of one year, yielded a temperature of 25°C.

There is no theoretical justification for extrapolation of a linear temperature scale over a wide temperature range. All chemical processes follow an Arrhenius exponential equation:

$$k = A \cdot \exp(E_a / RT)$$

where

- k is the rate constant for the process
- A is a constant (the Arrhenius pre-exponential factor)

$E_a$  is the Arrhenius activation energy  
 $R$  is the gas constant  
 $T$  is the temperature in degrees Kelvin

From the Arrhenius equation, a plot of  $\log(k)$  versus  $1/T$  will yield a straight line. In the initial stages of the reaction, provided the effective concentration of reactants does not change, these may be considered to be constant. A pseudo rate constant may be obtained from the inverse of the time to form a fixed concentration of products. A plot of the logarithm of this pseudo rate constant versus  $1/T$  will yield a straight line from which the activation energy may be calculated.

An Arrhenius plot of the data from Reference 17 at 43.3°C and 80.0°C is shown in Figure 1. The line has been extended to include calculated values for 1 to 4 years and to 150°C. All points on the line correspond to the same extent of reaction producing equivalent total insolubles formation. The calculated activation energy is 64.9 kJ mol<sup>-1</sup> (15.5 kcal mol<sup>-1</sup>). An ageing period of 3 months (91 days) at 43.3°C is generally accepted as being equivalent to one year of ageing at "ambient temperatures". From Figure 1, it may be noted that the equivalent temperature for 1 year of ageing is at the relatively high "ambient temperature" of 26.4°C. Using an "ambient temperature" of 18.7°C, 91 days ageing at 43.3°C is equivalent to 2 years ageing, whereas if 11.3°C is the reference "ambient temperature", the ageing at 43.3°C is equivalent to 4 years ageing.

The activation energy calculated from the line in Figure 1 of 64.9 kJ mol<sup>-1</sup> is at the upper end of the range of values (40–60 kJ mol<sup>-1</sup>) reported for the formation of insolubles from 2,5-dimethylpyrrole [18]. It is also greater than the value of 38 kJ mol<sup>-1</sup> reported for the catalysed polymerization of n-butyl vinyl ether by hydrogen iodide/iodine [19] or by a metal sulphate-sulphuric acid complex [20]. The most likely systematic error in the value of the activation energy arises from a mechanism change as reactions with greater activation energies make greater contributions to the overall mechanism at the higher temperatures. The effect of these contributions is to increase the calculated activation energy. Evidence for this is seen in the 150°C data from Reference 17. The calculated equivalent time at 150°C is 4.3 hours, whereas the experimental time is 1.5 hours. The calculated activation energy using the data at 43.3°C and 150°C is 76.0 kJ mol<sup>-1</sup>, 11.1 kJ mol<sup>-1</sup> greater than the value from the data in Figure 1.

### 3.2 Filterability

There is no universally accepted standardized test to determine the rate at which a fuel may be filtered. Many non-standardized tests have arisen to determine the relative filterability of fuels and there are two basic approaches. The most widely used are measurement of the time to filter a fixed volume of fuel through a defined filter medium using a fixed pressure differential or a uniform variable pressure differential across the medium. A fixed pressure differential arises from pressure or vacuum filtration whereas a uniform variable pressure is obtained by the gravity filtration of an initially constant head of fuel. In both cases, the filtration time is compared to that for a standard fuel, often the test fuel which has been pre-filtered. The procedure described by Onion and Bartlett makes use of a variant of the gravity feed procedure [21]. An alternate procedure determines the rate of pressure increase across a filtration

membrane at a fixed flow rate through the membrane. Apparatus for this method is described in the UK DEF STAN 91-4/5.

In this report, relative filterability was determined using a fixed pressure differential. The filtration time was converted into a Filtration Index (FI) by division with the filtration time for the unaged fuel through the filter medium. The filtration time of pre-filtered fuel in this study was  $90 \pm 5$  seconds for 100 mL. The reproducibility of the filtration times for duplicate samples of aged fuel showed greater variability than for unaged fuel. Formation of variable-sized particulate matter during ageing of duplicate samples, and non-uniformity in the performance of the nominal pore size filter membranes with filtration of contaminated liquids, may have contributed to variations.

Filtration times for duplicates were averaged and converted into the FI for semi-quantitative filterability evaluation. Aged fuels with FI values between 1.0 and 1.3 were considered to have "good" filtration characteristics, between 1.3 and 2.0 "fair", and greater than 2.0 were considered "poor". The absolute magnitude of the FI is a function of the volume of fuel filtered per unit area of filter medium. With larger filtration volumes, the relative magnitude of the FI values is increased for fuels with filter blocking particles. Thus FI values cannot be considered absolute but are a function of the experimental conditions.

#### 4. RESULTS

##### 4.1 Ageing at 43.3°C

Mild accelerated ageing of fuels at 43.3°C is widely accepted as being the most realistic and accurate test for estimation of the long term stability of diesel distillates during bulk storage [3]. The data in Figure 2, therefore, are considered to be the most representative of the performance of PU foam fuel stabilizing additives under field conditions. Ageing at 43.3°C generally requires relatively long trial periods (at least 13 weeks) for significant changes in the fuel to occur and results shown in Figure 2 were obtained after 26 weeks.

It is evident that PU foams greatly reduced the amount of both suspended and adhered particulate matter. In many runs, the total insolubles levels were close to experimental detection limits, indicating very high fuel stability compared with the aged reference fuel. Polyether foam #1 underwent slight physical disintegration during protracted fuel immersion, with visible foam fragments contributing to the particulate component, thus increasing total insolubles. This, however, was the only foam in this run which was not designed specifically for fuel immersion; all other foams showed unaffected structural integrity.

The FI for all fuels aged at 43.3°C are shown as the top graph in Figure 2. Values were equivalent to that for the unaged reference fuel (1.0) within experimental error, with the exception of foam #1, for which there was a slight decrease in filterability. By comparison, the aged reference fuel had a significantly higher Filtration Index of 1.6.

Weight percent increases of PU foam samples after fuel ageing were in the range 2.2 to 3.8. In each case, absolute weight increases of foams exceeded the reductions in total insolubles, effected by the immersed foams, by a factor of between two and three fold. For example, the weight increase (per litre of fuel) of foam #10 was 141 mg, whereas reduction in total insolubles, relative to the reference fuel, was 47 mg/L.

Relatively modest improvement in aged fuel blend colour was effected by the PU foam additives, compared with the reference fuel. It has been stated previously [22] that the colour rating of a fuel gives little indication of the degree of fuel degradation with respect to total insolubles formation and this finding is again evident.

#### 4.2 Ageing at 80°C and 120°C

The effect of ageing fuel at 80°C for 7 days is shown in Figure 3. Again, the presence of PU foam significantly decreased the total amount of insolubles formed compared to fuel aged without foam. From the Arrhenius plot of Figure 1, ageing for 7 days at 80°C is equivalent to 13 weeks ageing at 43.3°C. On this basis, the fuel samples represented in Figure 2 were aged for the equivalent of twice the period of those in Figure 3. However, the amount of total insolubles for all solutions in Figure 3 was greater than that for those in Figure 2. The reasons for this are not clear although it may be noted that the series of runs in Figure 3 was carried out after all the other experiments described in this report. Degradation of the LCO during successive thawing and refreezing from storage at -20°C or the SRD (stored at ambient temperature) may have been a contributing factor. In an earlier experiment, a similar blend of these fuel components at 80°C for 14 days yielded 6 mg less total insolubles and had a FI of 2.2.

The FI results shown in Figure 3 may all be classified as poor compared to the unaged reference fuel. Part of the explanation for this may follow from previous reports that the relative filtration time of aged fuel passes through a maximum and then decreases on continued ageing, although the amount of total insolubles continues to increase [8]. This is possibly due to a variation in the filter clogging properties of the particles as the average size varies with age. The lack of any direct correlation between amount of particulate matter and fuel filterability is also shown in Figure 3. The experimental fuel with the greatest amount of suspended particulate matter had the least filter clogging tendency. The larger amount of material may have allowed a greater combination of smaller particles. However, the fuel with the second largest amount of suspended particulate had the poorest filterability. This was a fuel containing a high resilience foam (foam #5) with a very low air permeability. It is probable that the flow of fuel through the foam was also low.

Comparison of ageing at 80°C and 120°C as shown in Figure 4, indicates that for all experimental fuels the amount of total insolubles increased by more than twofold at the higher temperature. From the Arrhenius plot in Figure 1, ageing for 13 days at 80°C is equivalent to 2.5 days at 120°C. However, the amount of total insolubles obtained for all fuel samples aged at 120°C is greater than would be expected from the Arrhenius plot. This is possibly due to a variation in mechanism for the deposit forming processes at the higher temperatures in which a greater contribution from processes with larger activation energies will result in more particulate being produced than would be calculated from the Arrhenius expression.

Some thermal degradation of foam #1 (a polyether PU foam) was apparent under the severe ageing conditions of 120°C for three days. The filtered particulate matter contained visible cellular fragments which had broken from the foam sample in addition to insoluble organic particulate matter. This was confirmed by the observed net weight % loss of the foam after the fuel stress. As the foam fragments contributed to the particulate matter, the total insolubles from fuel ageing reactions should have been less and the improvement in fuel stability greater than shown in Figure 4. There were no apparent cellular fragments from the thermal degradation of polyester PU foam #2 under similar ageing conditions. Similarly, in the experiments at 43.3°C and 80°C there was no visual evidence for thermal degradation of the other PU foams. PU foam #1 was not manufactured for use in fuel and this may have contributed to its instability in the ageing experiments at 120°C.

### **4.3 Comparison with Fuel Soluble Stability Additives**

Figure 4 compares graphically the effect upon the ageing of fuel at 80°C and 120°C of the Du Pont distillate fuel stability additives FOA#3 and FOA#15 at a concentration of 24 ppm with that for PU foam. In a previous study using a similar fuel blend, reductions in total insoluble matter in the range 50-70% were achieved with FOA#3 at the same concentration [5]. The reductions in this study were of a similar order for ageing at both 80°C and 120°C. Compared to the FOA#3 additives, greater reductions in total insolubles were obtained with the FOA#15 additive, which in turn was not as effective as PU foams #1 and #2. Previously, the relative effectiveness of FOA#3 and FOA#15 has been shown to be variable [8]. For most experimental conditions in that study, FOA#3 was more effective in reducing the total insolubles matter and the filtration index. This variability was postulated to be associated with the effect of the dispersant component in FOA#15.

It may be noted in Figure 4 that the FOA#3 and FOA#15 were most effective in reducing the amount of suspended particulate matter in the aged solution, whereas the amount of adhered particulate was actually increased compared to the reference fuel without additive. PU foam was effective in reducing the amounts of both suspended and adhered particulate.

### **4.4 The Effect of Fuel Destabilizing Agents**

#### **4.4.1 Copper Naphthenate**

Addition of copper (as copper naphthenate) to the reference blend at a concentration of 0.25 mg/L caused an increase in total insolubles from 39 mg/L (with no additive) to 70 mg/L, during ageing at 80°C for 13 days (Figure 5). The effect of copper in promoting deposit formation was not increased when the copper concentration was increased to 1.00 mg/L. The ratio of suspended to adhered particulate was similar to that for aged fuel not containing copper, with most being suspended in the solution. As for the earlier experiments, the increase in total insoluble matter in the presence of copper ions compared with the reference solution did not increase FI values.

In the presence of PU foam, ageing of the 0.25 mg/L solution of copper in fuel decreased total insolubles formation by 89%. The amount formed (8 mg/L) was the

same as for the reference fuel (no copper added) aged with PU foam, indicating that the action of the copper had been fully counteracted by the foam. With the 1.00 mg/L copper solution, the foam was slightly less effective, giving an 81% reduction in insolubles. However, the performance of PU foam as an efficient copper deactivator is evident. Significant improvements in FI values were also achieved when the copper solutions were aged with PU foam samples.

#### 4.4.2 Chloroacetic Acid

It may be seen from Figure 6 that chloroacetic acid (0.001 M and 0.003 M) in the fuel blend significantly increased the amount of total insolubles compared with the reference fuel. Respective increases in total insolubles of 2.4 and 3.6 fold at the two acid concentrations were obtained. Immersed PU foam additives effectively counteracted the destabilizing effect of the chloroacetic acid to a degree similar to that for the copper naphthenate. In combination with PU foam additive, particulate was reduced by > 80% for the acid/fuel solutions, and improved FI values were observed (2.6 : 1.1 for 0.001 M solution, 2.6 : 1.8 for 0.003 M solution).

#### 4.4.3 Benzenethiol

Addition of benzenethiol to the fuel blend, at concentrations of 0.001 M and 0.003 M, caused very large increases in total insolubles from 43 mg/L, for the undoped fuel, to 217 and 600 mg/L, respectively, during fuel ageing at 65°C for 43 days (Figure 7). The effect of benzenethiol is unique in that the particulate is formed almost exclusively as adhered material. The absence of suspended particulate matter is seen in low FI values for all solutions containing benzenethiol.

Dramatic reductions in total insolubles were achieved when PU foam samples were immersed in the solutions of benzenethiol in the fuel. The magnitude of insolubles reduction (> 98%) indicated that the powerful deposit promoting activity of the thiol had been completely counteracted by the PU foam additive. Weight percent increases of 7.3 and 12.3, respectively, for the foam samples used in the 0.001 M and 0.003 M benzenethiol solutions were relatively higher than those observed (2-4%) for foams in fuels aged in the absence of a deposit promoter. Absolute increases in foam weights (mg/L), however, were significantly less than the reductions in total insolubles caused by the foams.

#### 4.4.4 1-Hexadecanethiol

The aliphatic mercaptan, 1-hexadecanethiol, had an inhibiting influence on formation of total insolubles, when added to the reference blend at a concentration of 0.001 M (Figure 8). This effect, which was more pronounced at a thiol concentration of 0.003 M, was opposite to that found for the aromatic thiol, benzenethiol, as discussed above.

Aliphatic thiols have been found by other workers [6, 23] to have an unpredictable influence on fuel stability. In the presence of aromatic thiols from

catalytically cracked distillates, they exerted an inhibitory influence, whereas in highly refined SRD mixed with cracked distillates, from which aromatic thiols had been removed, they caused a pronounced increase in deposit formation [6]. In other studies, using hydrogenated jet fuel, an aliphatic thiol reduced oxygen uptake and deposit formation by the fuel at elevated temperatures when the concentration of the thiol was in the range 0.001 M - 0.003 M, similar to that used in the present study. At lower and higher thiol concentrations, however, these effects were reversed [23].

Notwithstanding this inconsistent behaviour, the effect on fuel ageing of PU foam additives in the presence of 1-hexadecanethiol was similar to that described in all the preceding ageing experiments. Total insolubles were reduced to low levels in the presence or absence of thiol, and Filtration Index values were also markedly improved (Figure 8). It may be noted that the filterability of the thiol containing fuel deteriorated with increasing thiol concentration in the reference blend, even though total insolubles, as well as particulate levels, had been reduced. This would again suggest that aggregation of particles as more are formed in the solution increases the ease of filtration.

The 1-hexadecanethiol also imparted to the aged fuel a significantly worse colour rating of 7.0 (ASTM D1500), compared to the other fuel-soluble additives in aged fuels (colour : 4.5-5.5). Furthermore, the PU foam caused a marked improvement in the colour (4.0-4.5) of the fuel/thiol solution, compared to only marginal improvements in conjunction with other additives.

#### **4.5 Pretreatment by Initial PU Foam Immersion**

Single pretreatment of fuel at ambient temperature for five days resulted in a reduction of the total insolubles of 39% from 39 mg/L to 24 mg/L (Appendix E). Fuel samples which had been treated twice with PU foam, firstly at ambient temperatures followed by fresh PU foam at 120°C for 3 or 7 hours gave reductions in total insolubles of 41% and 62% respectively. Single pretreatments of the fuel with foam at 120°C for periods of 3 and 7 hours were ineffective in reducing insolubles, when the fuel was subsequently aged at 80°C for 14 days. These results indicated that the pretreatment at ambient temperatures had provided a beneficial effect on fuel stability, while pretreatment at 120°C was ineffective when not preceded by ambient treatment. These results may be explained by an equilibrium between the foam and particulate precursors [24].

#### **4.6 Repeated Ageing of PU Foams**

Samples of foams #1 and #2, which were aged successively with aliquots of fresh fuel for two periods of three days and a final period of four days at 120°C, were still effective in reducing total insolubles, colour and FI at the completion of the series. In fact, both foams performed marginally better in the second run than in the first. The increased severity of the third run was shown by an increase in total insolubles in the reference fuel from 129 to 177 mg/L (Appendix F). Some minor disintegration of foam #1 occurred in the third run due to thermal instability as described earlier, with PU foam cells contributing to the weight of insoluble matter. A corresponding increase in FI was observed, but the value was still significantly lower than that for the aged reference fuel. From Figure 1 it may be shown that the total period of

ageing at 120°C was equivalent to 7.4 years or 14.8 years ageing at ambient temperatures of 26.4 or 18.7°C, respectively. At the completion of the series, foam #2 still gave a reduction in total insolubles of 80%.

#### **4.7 Mass Variations of PU Foam Samples**

For all fuel ageing experiments with PU foam there was a measured mass increase in the foam (see Appendices). This was in the range 1.5-3.6% except for 120°C experiments with Foam #1, for which a small amount of disintegration of the foam occurred. Excluding these, the increase was two to five times the decrease in the total insolubles in the aged fuel, compared to a reference fuel aged without foam. Clearly, additional material to that by which the total insolubles decreased was incorporated with the foam. For many of the experiments reported in the Appendices, the mass of soluble gum by the method of steam jet evaporation (ASTM D381) was determined in the aged fuel. Values of soluble gum in the range 150-300 mg/L were obtained, but variations showed no correlation with the presence or absence of PU foam and the results for soluble gum are not reported here.

### 5. DISCUSSION

#### **5.1 Formation of Total Insolubles**

Acid catalysis is a significant factor in the rate of formation of insoluble particulate matter in distillate fuel [5]. The chemical reactions which are actually catalysed by naturally occurring acids in fuels have not been completely identified, but there is little doubt that they involve heteroaromatic compounds present in unstable fuels [6, 15, 25]. Addition of organic acids or benzenethiol to the experimental fuels substantially increased the amount of total insolubles upon ageing of the fuel. Measurement of the thiol concentration by ASTM D3227 showed that the thiol concentration decreased below detection limits in less than 10% of the ageing period. This supports previous work [26] that aromatic thiols are oxidized to sulphonic acids which are active catalysts for the formation of insolubles in distillate fuel [5]. Consistent with this theory is the experimental data that showed that the addition of 1-hexadecanethiol did not increase the formation of insolubles. Oxidation of 1-hexadecanethiol to a more acidic sulphonic acid is a high energy process.

#### **5.2 Effect of PU Foam Upon Total Insolubles**

The presence of PU foam reduced the amount of total insolubles formed compared to the reference fuel during the ageing of all fuel samples investigated in this study. The fuels contained 30% unhydrogenated LCO as previous work has shown that presence of unhydrogenated LCO is a major factor contributing to the formation of particulate matter in distillate fuel [5]. Total insolubles in many of the aged fuel samples containing PU foam approached those of unaged fuel. The 43.3°C fuel ageing (Figure 2) is considered to most closely approximate conditions of fuel storage

at ambient temperature [3] and in all but one of the eight aged fuel/foam systems, total insolubles were 3 mg/L or less compared to 49 mg/L for the reference fuel.

### 5.2.1 With Previously Degraded Fuels

Samples of two diesel fuels which had deteriorated significantly during ambient ageing in bulk storage facilities were treated with PU foam #13. The levels of suspended organic particulate matter in the fuels, fuel filterability and colour were measured after the fuels had been in contact with foam under mild ageing conditions. It is evident from the results shown in Table 3 that the foam has had a most beneficial effect in restoring the quality of the fuels. In its absence, the quality of both samples became significantly worse under the mild accelerated ageing conditions used. Various foam/fuel ratios were used, and it was found that only 0.2% wt. vol. was needed to markedly improve the quality of Fuel B in just 3 weeks at 43.3°C. Fuel B was known to have been causing serious engine malfunctions in heavy duty tracked vehicles because of its high tendency to rapidly block fuel filters. After treatment with the PU foam, the fuel was considered to have been suitable for further use in vehicles.

Unlike fuel soluble additives, PU foam has been found to have the capability of removing suspended organic particulate material from a fuel without external filtration. Restoration of large volumes of degraded fuel by filtration is not generally feasible because an empty tank of equal volume would be required nearby for transfer of the filtered fuel. Recirculation filtration is an inherently inefficient process, and shipment of deteriorated fuel back to the refinery for redistillation is not cost effective. Therefore, fuel which has become contaminated by formation of organic particulate during storage, and is no longer fit for use in diesel engines, is often downgraded and disposed of for use in less demanding applications. PU foam thus offers the potential for improving fuel quality in situ with large volume storage tanks.

### 5.2.2 With Carboxylic Acids

Carboxylic acids are naturally occurring minor constituents of crude and refined petroleum. At the levels normally found in distillate fuel, the catalytic effect of the carboxylic acids upon the formation of insolubles is small. It is postulated that a preliminary process for accelerated ageing of distillate fuel is the formation of carboxylic acids and other oxygenated species by oxidation of the fuel. Addition of carboxylic acids supplements this preliminary oxidation process. In this and previous studies chloroacetic acid has been used due to its higher acidity (lower pKa value) compared to its aliphatic hydrocarbon analogues. As a result, it is a more powerful deposit promoting agent [5]. Despite this property, PU foam was found to be effective in suppressing insolubles formation in 0.001 and 0.003 M solutions of the acid in the fuel blend (Figure 6). It may be assumed from these results that the foam would be at least as effective in counteracting the effect of the less acidic carboxylic acids naturally present in fuel.

### 5.2.3 With Thiols

The fuel blend components used in this study were derived from Australian Bass Strait crude, which has a low sulphur content. Crudes from other regions, however, can have much higher sulphur contents, and contain appreciable amounts of various sulphur-containing components [23]. Benzenethiol is a powerful deposit promoting agent in LCO fuel blends. It is readily oxidized to the disulphide and may be removed by refinery processes involving mild hydrotreatment or caustic washing. However, in untreated LCO blends aromatic thiols contribute to deposit formation. In this study it has been demonstrated that the presence of PU foam in fuel during ageing completely counteracted the effect of benzenethiol when it was added to the fuel blend at concentrations up to 0.003 M (Figure 7). The reduction in total insolubles formation was 99%, compared to 80% reduction when a similar fuel blend containing 0.003 M benzenethiol was aged in the presence of 96 mg/l of the commercial liquid additive FOA#3 [5].

### 5.2.4 With Soluble Copper

The use of copper components in distillate fuel systems has long been known to cause fuel instability [27]. Copper may increase the rate of oxidation of hydrocarbons and other components to species which produce insolubles either directly or by catalytic action. The copper may also directly catalyse the formation of insolubles by phenolic oxidative coupling [14]. Fuel solutions of copper naphthenate (0.25 - 1.00 ppm as Cu) were effectively stabilized by PU foam, with total insolubles being reduced to levels similar to those obtained with the same foam/fuel system, but in the absence of added copper (Figure 5).

### 5.3 Effect of PU Foam Upon the Filtration Index

Total insolubles are the prime indication of degree of degradation of distillate fuel due to ageing. The FI is independent of the amount of adhered particulate matter, so the correlation with total insolubles would be expected to be poor. The FI would be expected to be dependent only upon the amount and type of suspended particulate. PU foams have been shown to reduce the amount of suspended particulate matter in aged fuels, but the correlation between the FI and the amount of suspended particulate matter is not linear. Fuel containing a small number of large particles would filter relatively rapidly (FI decreasing towards 1.0) compared to a similar fuel containing a lower mass but a greater number of smaller particles. Within a series of experiments conducted at constant temperature and ageing time, the overall trend is for a decreasing FI to correlate with decreasing amount of suspended particulate matter. From this trend, the general effect of the presence of PU foam in aged fuel is to reduce both the amount of suspended particulate matter and the FI. However, a number of exceptions may be seen in the Figures, in which solutions containing relatively high amounts of suspended particulate matter may have lower FI values than solutions with lesser amounts of suspended particulate. These variations may be explained by the changing distribution of particle sizes in the aged fuels. The particle size distribution of the suspended particulate matter is currently being investigated.

## 5.4 Mechanism of Fuel Stabilization by PU Foam

### 5.4.1 Modification of Chemical Equilibria

All PU foams contain urethane N-H and C=O functional groups [28] which undergo extensive hydrogen bonding [29]. A wide range of organic and inorganic substances are extractable by PU foams [30], and mechanisms for interaction of foam with fuel components are proposed:

- (a) Adsorption of chemical precursors of organic particulate matter by the foam.
- (b) Adsorption of dissolved particulate molecules by the foam to displace the solubility equilibria for formation of particulate matter.
- (c) Adsorption or solubilization of fuel degradation solid organic particulate matter on to the surface and into the interior of the foam.
- (d) Adsorption and interaction with polar species in the fuel to modify the acid/base environment.

The size or number of foam pieces has no apparent effect upon the fuel stabilizing properties of the foams. Similar results are obtained with a single piece of foam and an equivalent mass pulverized to a powder. Withdrawal from fuel on to the foam, by mechanism (a), of precursors of organic particulate would increase fuel stability. For example, phenols have been found to contribute directly to formation of insolubles in distillate fuel by phenolic oxidative coupling [14, 15, 27, 31], and reduction in phenol concentration would reduce their contribution to particulate matter. In associated studies, adsorption equilibria between phenols and other acidic molecules with polyurethane foams are being investigated in hydrocarbon solvents [24]. Concentrations of these species in solution are reduced significantly by the presence of PU foams.

### 5.4.2 Deposition of Insolubles on PU Foams

Mechanisms (b) and (c) may contribute to the fuel stabilizing properties of PU foams, through a process of adsorption and deposition of dissolved and insoluble fuel degradation products. Once organic particulate precursor material is deposited on or dissolved in the PU foam, it is not available for the formation of suspended particulate in the solution or adherent matter on the container. PU foams which were initially pale coloured, turned dark brown during fuel ageing. This coloration was very similar to that normally found for the filtered particulate matter and adherent gum from the aged reference fuel. Similar foam coloration occurred in experiments in which foam was used to absorb particulate matter which had formed in previously aged fuels (Table 3) and the results of those experiments provided strong evidence in support of mechanisms (b) and (c).

Mass increases were observed for foam samples after the fuel ageing experiments. However, these increases significantly exceeded the reductions in total insolubles for most experiments. It was likely that substances in addition to adsorbed insolubles and fuel particulate precursors are associated with the mass increase of the foam. Methylene chloride extracts of the aged foam #13, were examined by GC and GCMS and found to contain aromatic hydrocarbons. The majority of these were

alkylnaphthalenes, with distribution ratios similar to those in the fuel blend. Their presence in the foam would be explained by swelling normally encountered with PU foams in fuels containing aromatic hydrocarbons. An infrared spectrum (Figure 9) of the evaporated methylene chloride extract showed absorptions for aromatic C-H stretching ( $3060\text{ cm}^{-1}$ ) and out-of-plane bending ( $850\text{--}700\text{ cm}^{-1}$ ) which were characteristic of the aromatic hydrocarbons identified by GCMS. It is clear from the spectrum, however, that there is a significant contribution from other substances. The majority of the remaining absorptions are at frequencies characteristic of those for filterable particulate obtained from similar aged distillates [5, 31]. They also bear some similarities to spectra of phenolic extracts of similar fuel blends [5, 15].

Further evidence for the importance of particulate deposition on the foam is seen from the results for the ageing experiments with benzenethiol (Appendix C). As the benzenethiol concentration in the experimental fuel was increased from 0 to 0.001 and 0.003 M, the increase in mass of the PU foam after the ageing experiments was 72, 194 and 349 mg/L respectively. As the same mass of foam was used for each experiment, the mass increase for adsorption of fuel hydrocarbons would be expected to be constant. The additional foam mass increases in the presence of benzenethiol must therefore be due to processes outlined above.

#### 5.4.3 Acid Catalysis

Carboxylic acids are among the compounds adsorbed by PU foam [24]. Direct measurement of the adsorption of some carboxylic acids has shown this adsorption to be small. The decrease in chloroacetic acid concentration in the presence of foam did not vary the potential catalytic activity significantly. PU foams have urethane N-H and C=O groups which may have a buffering action in the fuel. However, these groups are only weakly amphoteric and are not likely to interact strongly with acid species in the fuel. Deactivation of acid catalysis does not appear to be a significant mechanism of fuel stabilization by PU foams.

#### 5.4.4 Comparison with Liquid Stability Additives

The liquid stability additives FOA#3 and FOA#15 were shown to be effective in reducing total insolubles (Figure 4). However, the amount of adhered particulate actually increased compared to the reference fuel, the overall decrease in insolubles being solely due to the reduction in suspended particulate matter. In this series of experiments, PU foam decreased both the suspended and adhered particulate matter compared with the aged reference fuel. This would provide further evidence that the prime action of liquid stability additives is to modify the acid-base composition of the fuel, whereas the prime action of PU foam is to reduce the concentration of deposit precursors and to act as an adsorption medium for the material which contributes to total insolubles in aged fuel. The multiplicity of stabilization mechanisms would explain the greater degree of fuel stabilization which was obtained with PU foams compared to liquid stability additives at the concentrations used in this study. It has been shown that, for FOA#3, the greater benefit is obtained in the 20-50 ppm range, with diminishing returns at higher concentrations [5]. The relative differential in efficiency and economy is similar for increased foam/fuel ratios.

#### 5.4.5 Soluble Stability Agents from PU Foam

It was considered possible that residual species from the manufacture of PU foams, such as tertiary amine polymerization catalysts and similar organic bases, may be extracted into the fuel and function in a manner similar to commercial liquid additives. This was investigated by refluxing PU foam with toluene for several hours and adding the toluene extracts to experimental fuel blends. No reduction in total insolubles was obtained in aged fuels containing the toluene extracts compared to solutions without additives.

### 6. CONCLUSIONS

#### 6.1 Effectiveness of PU Foams as Fuel Stability Agents

At the foam/fuel ratios reported here, all PU foams substantially reduced the amount of suspended and adhered particulate matter which is formed during the ageing of distillate fuels. For stabilization of distillate fuel in a field environment, reticulated polyether types are preferred. Three mechanisms have been proposed for stabilization:

- (a) Adsorption of chemical precursors of organic particulate matter by the foam.
- (b) Adsorption of dissolved particulate molecules by the foam to displace the solubility equilibria for formation of particulate matter.
- (c) Adsorption or solubilization of fuel degradation solid organic particulate matter on to the surface and into the interior of the foam.
- (d) Adsorption and interaction with polar species in the fuel to modify the acid/base environment.

Concentrations of molecules contributing to the formation of total insolubles on fuel ageing are very low. In the process of reducing insolubles formation in fuel, the PU foam itself is partly deactivated. Due to the much higher relative concentrations of PU foam compared to trace amounts of fuel insolubility precursors, the action of the PU foam is long lasting, being able to reduce insolubles formation in masses of fuel orders of magnitude of its own mass.

The action of PU foam in reducing the amount of suspended particulate matter and the colour of fuel which has been aged prior to being in contact with the foam is explained by mechanisms (b) and (c). Mechanism (a) may also contribute if the reactions contributing to the formation of particulate matter are reversible. As all equilibria which have been studied are exothermic [24], the adsorption of species by the three mechanisms is greatest at lower temperatures. However, the rate of reaction at these temperatures is slow and stabilization of pre-aged fuel by PU foam is a relatively slow process.

For most fuel samples, reductions in suspended particulate will decrease the filtration time for the fuel. However, there is not a linear relationship between rate of filtration and the amount of suspended particulate matter. The particle size and the characteristics of the particulate are also significant in determining the relative ease of filtration. For some experiments, although a reduction in total particulate was achieved, the relative filtration time increased.

## **6.2 Use of PU Foams with Hydrocarbon Fuels**

Flexible PU foams in general do not suffer significant structural damage when immersed in hydrocarbon liquids. Some swelling may occur with foams in liquids containing high levels of aromatics, but this effect is reversible when the foams are removed. Reticulated PU foams are manufactured specifically for hydrocarbon fuel immersion, mainly for fuel slosh attenuation, and explosion suppression properties [16]. Foams containing either polyether or polyester polyols can be fuel-compatible, but the polyether variety is considerably less susceptible to hydrolysis from the presence of water or alcohols in the fuel.

The principal current applications for these types of foams are in racing car and aircraft fuel tanks, because of inherently high vehicle velocities and the use of low flash point, high flammability fuels. There is, however, only limited application with diesel powered vehicles and equipment which use higher flash point (greater than 60°C) distillates and are generally run at relatively low speeds, where fuel slosh is not a problem. Furthermore, many diesel engines, such as electricity generators, are in static installations, with the fuel stored in bulk tanks.

It is in the area of distillate fuel storage stability that a major new application for PU foams is proposed. Problems arising from the formation of organic particulate matter in distillate fuel is of major concern to the petroleum industry. For the stabilization of distillate fuel, refinery hydrotreatment is the preferred treatment method compared to the addition of liquid chemical additives due to the higher level of protection that is achieved. However, the current operating costs of refinery hydrotreatment plants are greater than the cost of additives such as FOA#3. Even the cost of liquid additive treatment may be significant due to the large volumes of fuel that need to be treated.

PU foams offer the potential for a distillate fuel stabilization treatment which is more cost effective than both hydrotreatment and liquid chemicals [32, 33]. For fuel containing unhydrogenated LCO, the presence of PU foam has been shown to be effective in reducing the formation of insolubles over a wide range of conditions. The advantages which will arise from the use of PU foams as fuel stability agents are as follows:

- (a) Insertion of foams in fuel systems would provide a continuously efficient, passive environment for suppression of fuel instability during storage.
- (b) The foams would have the capability of maximizing storage stability of very unstable fuels, thereby placing less demand upon expensive refinery hydrotreating, or continuous addition of fuel-soluble stability additives.

- (c) PU foams are physically and chemically stable at normal temperatures of fuel storage. As they are non-toxic, no precautions would be required in their use. Fuel-soluble tertiary alkylamine additives are toxic and require protective equipment to be handled in their concentrated form.
- (d) PU foams are relatively inexpensive and expendable, and small foam/fuel ratios achieve effective suppression of particulate formation.

As stability agents, PU foams may fill the fuel tanks of vehicles and smaller power plants. In this form, the benefits of PU foam for explosion suppression will also be retained. However this is not the preferred method of application due to increased cost for additional foam and the difficulty of periodic replacement. For stabilization purposes it is proposed that the foam be inserted in fuel systems as a readily replaceable unit. For vehicle systems, this could be a disposable self-contained cartridge, similar to that used for vehicle oil filters. For larger storage tanks, cylinders of foam, possibly attached to manholes in the roof of the tank, may provide a ready means of inserting and removing PU foam.

The ability of PU foam to remove polar fuel instability precursors from fuel could reduce the formation of fuel injector deposits in gasoline, automotive diesel fuel and aviation turbine fuel. Deposits formed on injectors may severely disrupt spray patterns into the combustion chamber and greatly reduce the combustion efficiency. A reduction in combustion efficiency not only increases the fuel consumption, but the products of incomplete combustion may lead to further malfunction of the engine. Included in problems that may arise from incomplete combustion are engine coking, valve piston ring sticking, excess smoke in the exhaust and in the case of gas turbine engines, excess combustor liner temperatures. In addition to being a fuel stability agent in its own right, PU foam has the potential to be a carrier for other fuel additives. Biocides are one such additive, which when incorporated into PU foam, could reduce microbiological activity in the fuel.

Use of the material for the purposes which have been outlined in this report would be expected to bring considerable benefits to consumers of a wide range of fuel types. The ability of consumers to, in effect, have a fuel stabilization system in their fuel tank reduces the risk of serious degradation of the fuel system from the effects of unstable fuel. By continuing to "refine" fuel in the distribution and consumer system, refineries have the option of reducing the use of expensive refinery processes or the greater use of lower quality crudes. The cost benefits from these options to the petroleum industry are likely to considerably exceed the cost of installation of PU foam fuel stabilizing systems.

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**TABLE 1****Fuel Properties**

	<b>SRD</b>	<b>LCO</b>
Density at 15C (D1298)	0.837	0.856
Colour (D1500)	0.5	1.5
Distillation (°C) (ASTM D2887)		
5%	157	193
20%	207	249
50%	270	282
80%	305	313
99.5%	380	364
FIA (Vol %) (D1319)		
Aromatics	21.9	50.5
Olefins	2.0	5.5
Saturates	76.1	44.1
Hydrogen Content (%)	13.3	11.9
Sulphur Content (%)	0.095	0.125
Nitrogen Content (%)	0.002	0.490
Acid Number (D664)	0.027	-

SRD: Straight Run Distillate

LCO: Thermally Cracked Light Cycle Oil

**TABLE 2**

**Classification of PU Foams used in Fuel Stabilization Experiments**

PU Foam No	Foam Type	Polyol Type	Air Flow (m <sup>3</sup> /h)
#1	N <sup>a</sup>	Ether	N.D. <sup>d</sup>
#2	R <sup>b</sup>	Ester	N.D.
#3	R	Ester	38.1
#4	R	Ester	40.9
#5	H <sup>c</sup>	Ester	0.5
#6	N	Ether	2.5
#7	N	Ether	8.0
#8	R	Ester	N.D.
#9	R	Ester	26.4
#10	R	Ester	N.D.
#11	R	Ester	N.D.
#12	R	Ester	N.D.
#13	R	Ether	N.D.

<sup>a</sup> N = non-reticulated

<sup>b</sup> R = reticulated

<sup>c</sup> H = high resilience

<sup>d</sup> N.D. = not determined

**TABLE 3**

**Action of PU Foam on Degraded Fuel**

PU Foam g/L	Suspended Particulate mg/L	Filterability Def Stan 91-4/5 Annex A	Final Colour
<b>Fuel A: 4 weeks at 43.3°C</b>			
0	23 <sup>a</sup>	15.0 psi/35 ml <sup>c</sup>	4.0
1.2	8	15.0 psi/227 ml	3.5
<b>Fuel B: 13 Weeks at 30.0°C</b>			
0	17 <sup>b</sup>	15.0 psi/90 ml	4.5
2.5	3	15.0 psi/295 ml	3.5
<b>Fuel B: 3 Weeks at 43.3°C</b>			
0	21 <sup>b</sup>	15.0 psi/40 ml	4.0
2	4	14.0 psi/300 ml	3.5

- a. Suspended particulate in Fuel A before ageing: 20 mg/l
- b. Suspended particulate in Fuel B before ageing: 13 mg/l
- c. The filterability test measures the pressure drop over a 2  $\mu$ m glass fibre filter during constant flow filtration. Lower pressure increases with larger volumes of fuel filtered indicates improved fuel filterability.

FIGURE 1

Arrhenius Plot of Particulate Formation

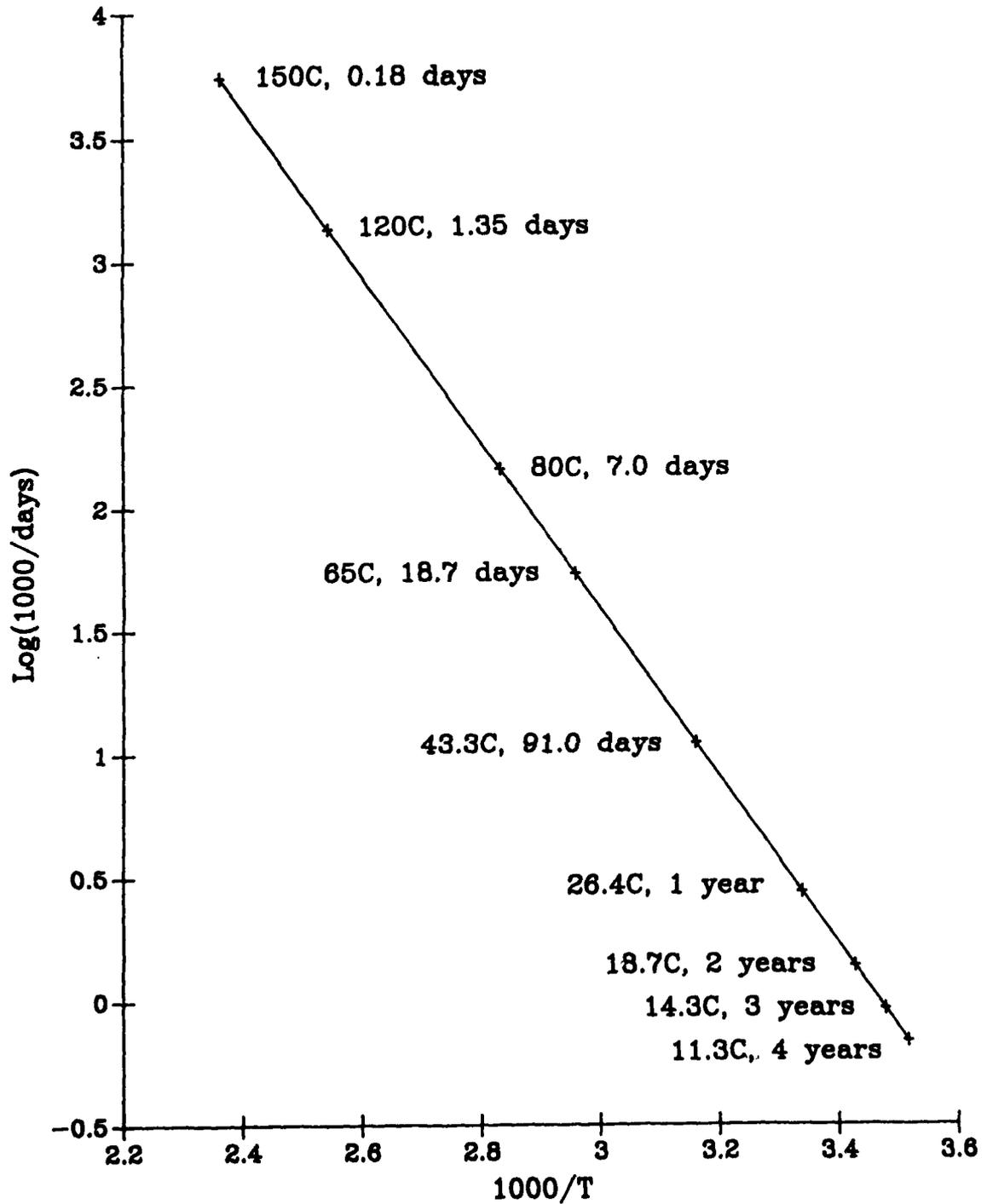


FIGURE 2

Effect of PU Foam Type  
Ageing 43C - 26 Weeks

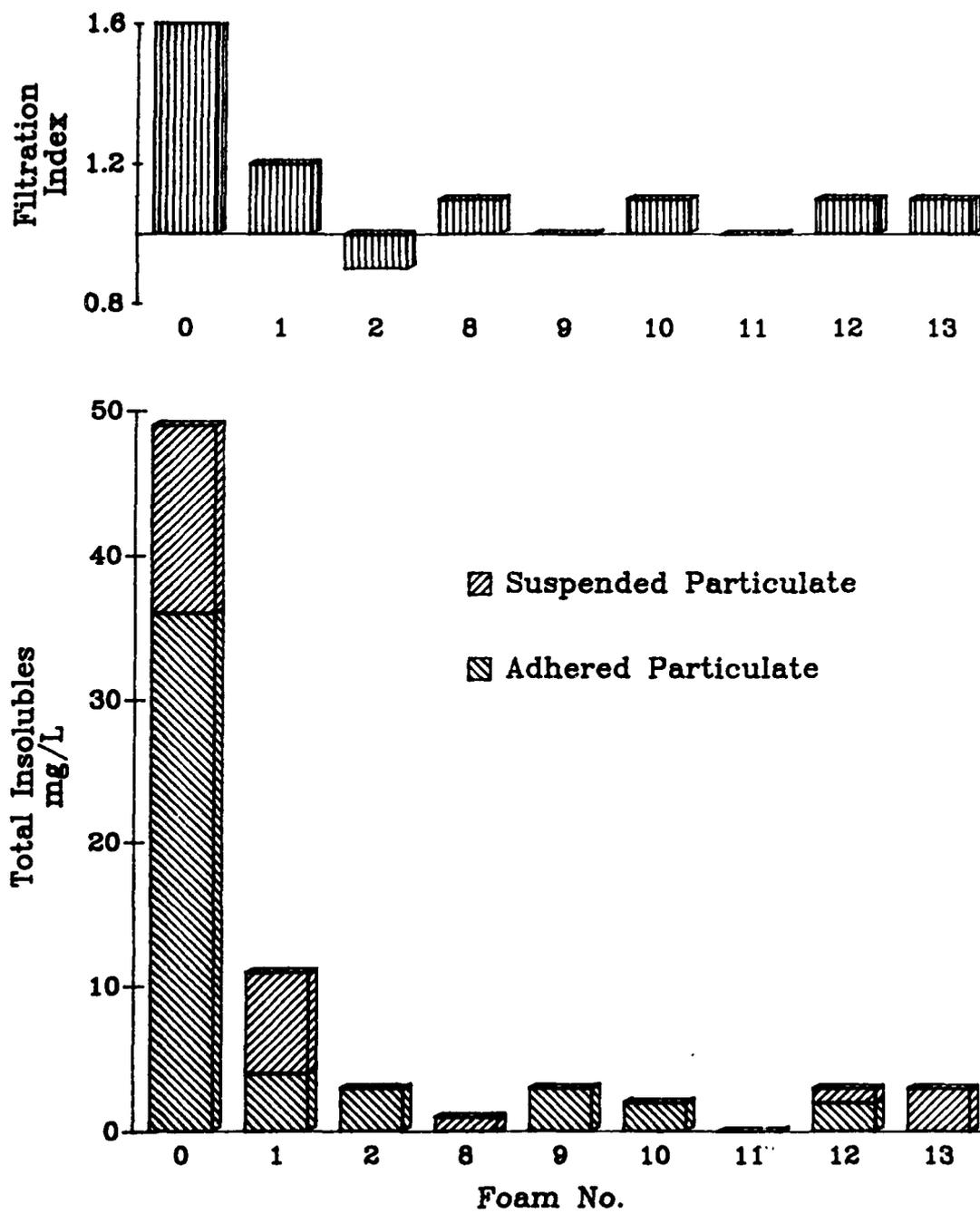


FIGURE 3

Effect of PU Foam Type  
Ageing 80C - 7 Days

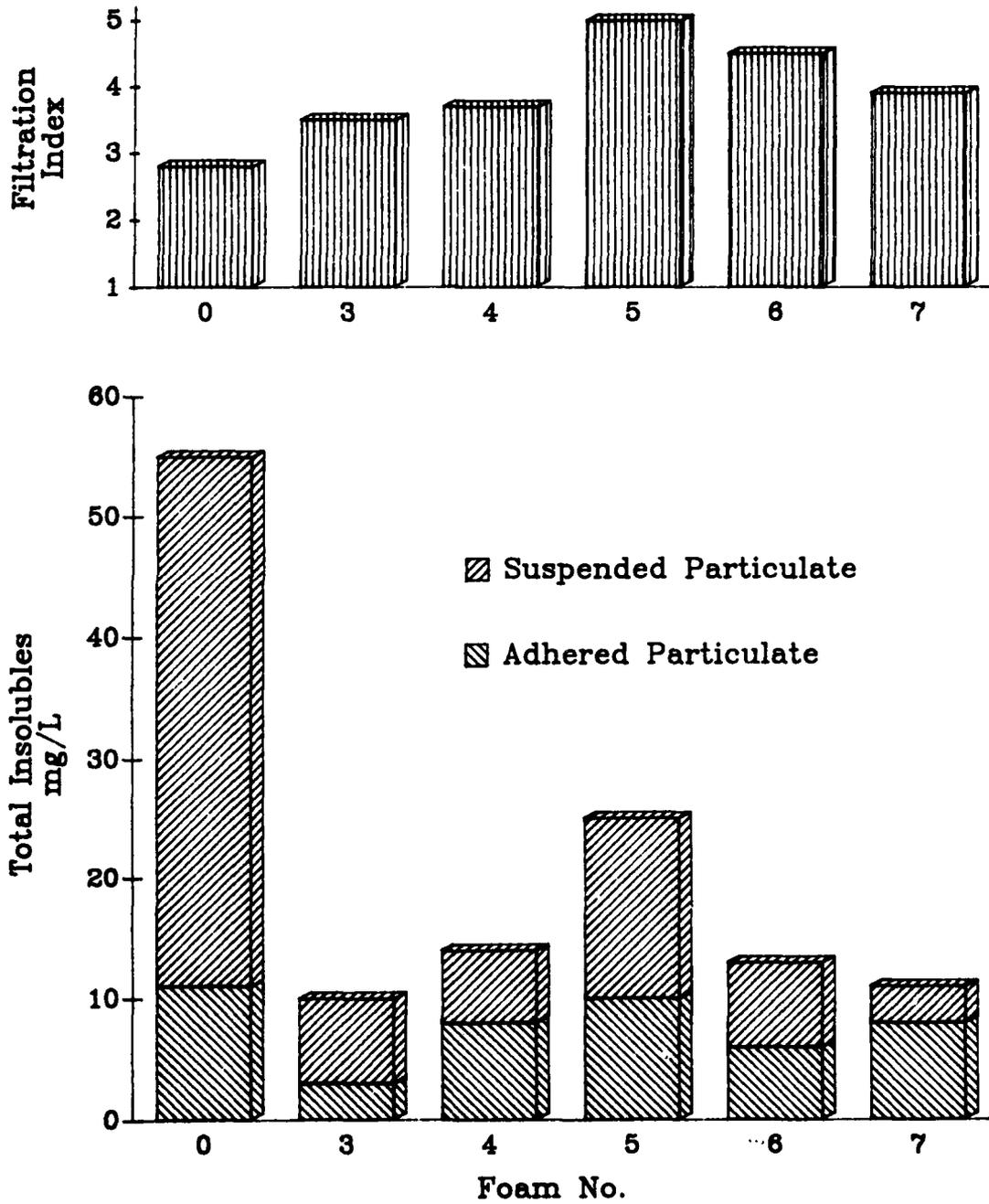
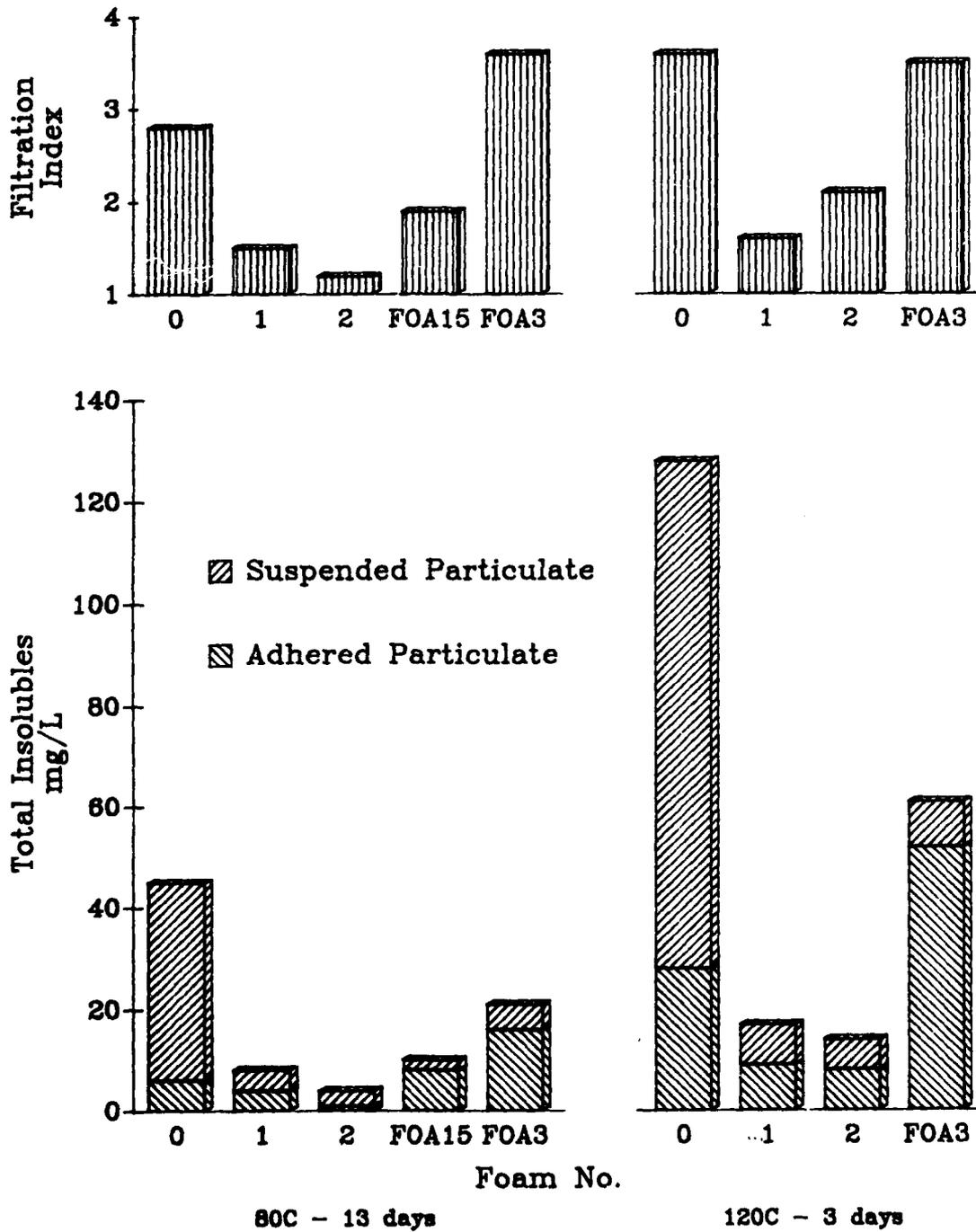


FIGURE 4

Comparison of Liquid Additives with PU Foam  
Ageing 80C - 13 Days and 120C - 3 Days



**FIGURE 5**  
**Effect of Copper Naphthenate**  
**Ageing 80C - 13 Days**

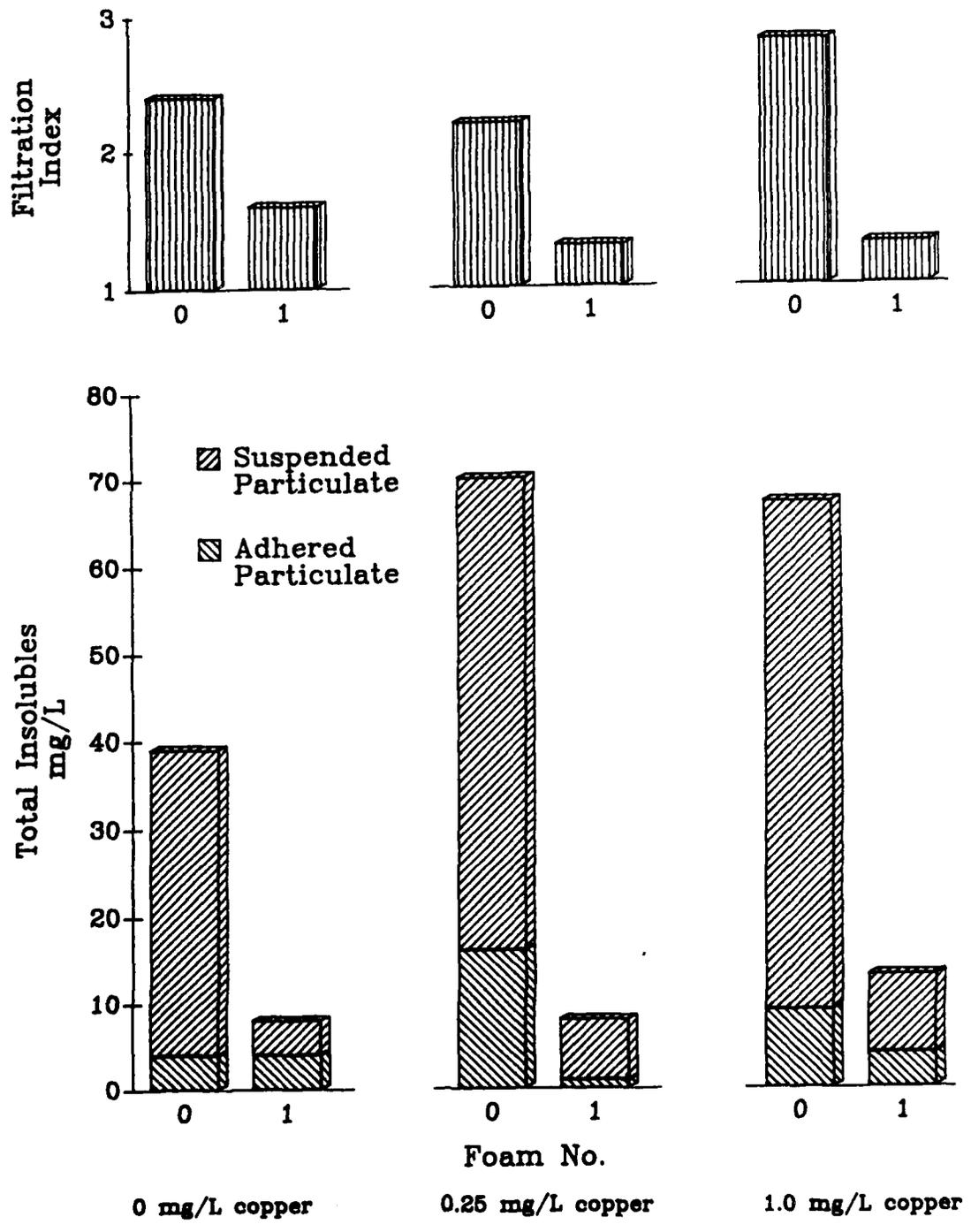


FIGURE 6

Effect of Chloroacetic Acid  
Ageing 65C - 43 Days

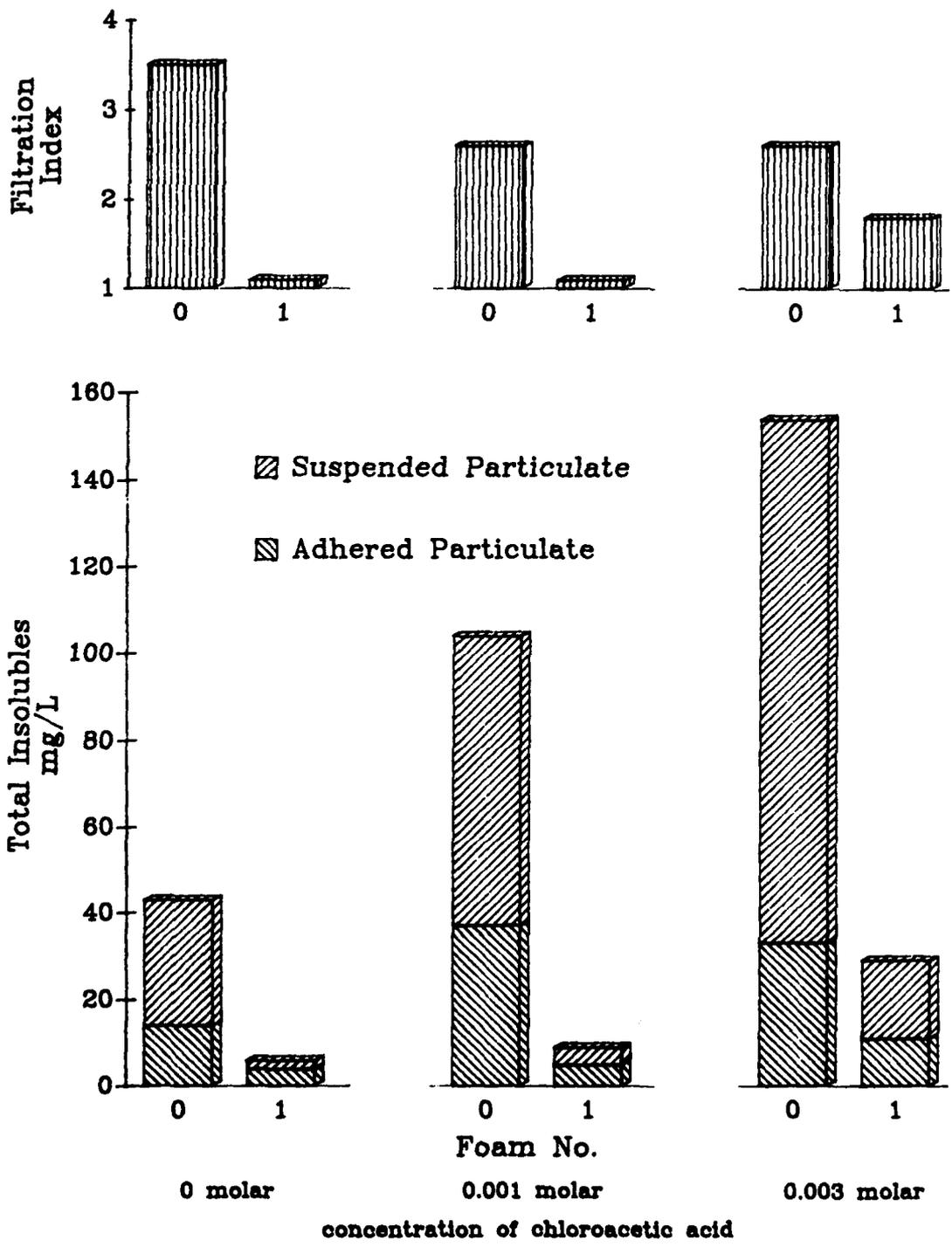


FIGURE 7

Effect of Benzenethiol  
Ageing 65C - 43 Days

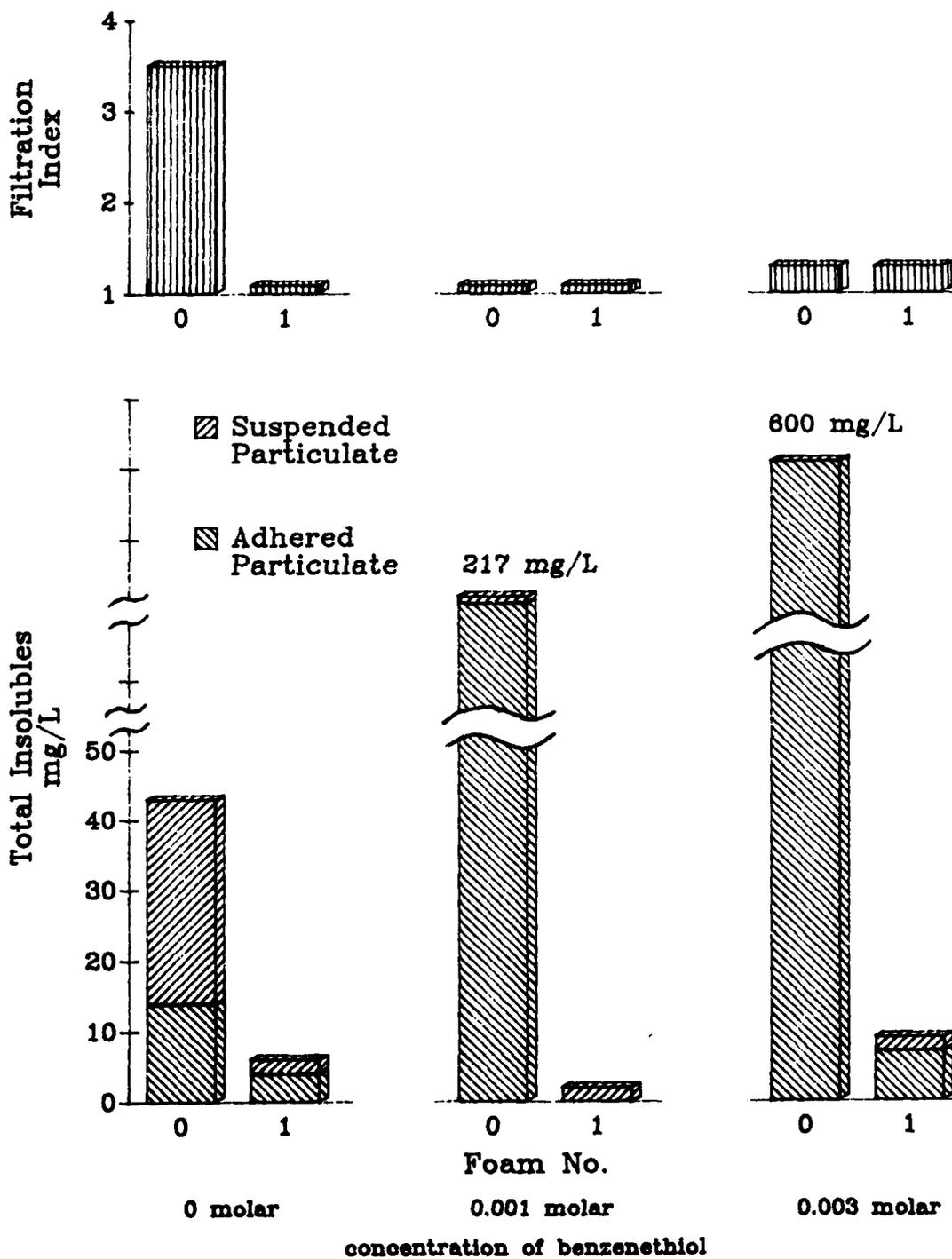


FIGURE 8

Effect of 1-Hexadecanethiol  
Ageing 65C - 43 Days

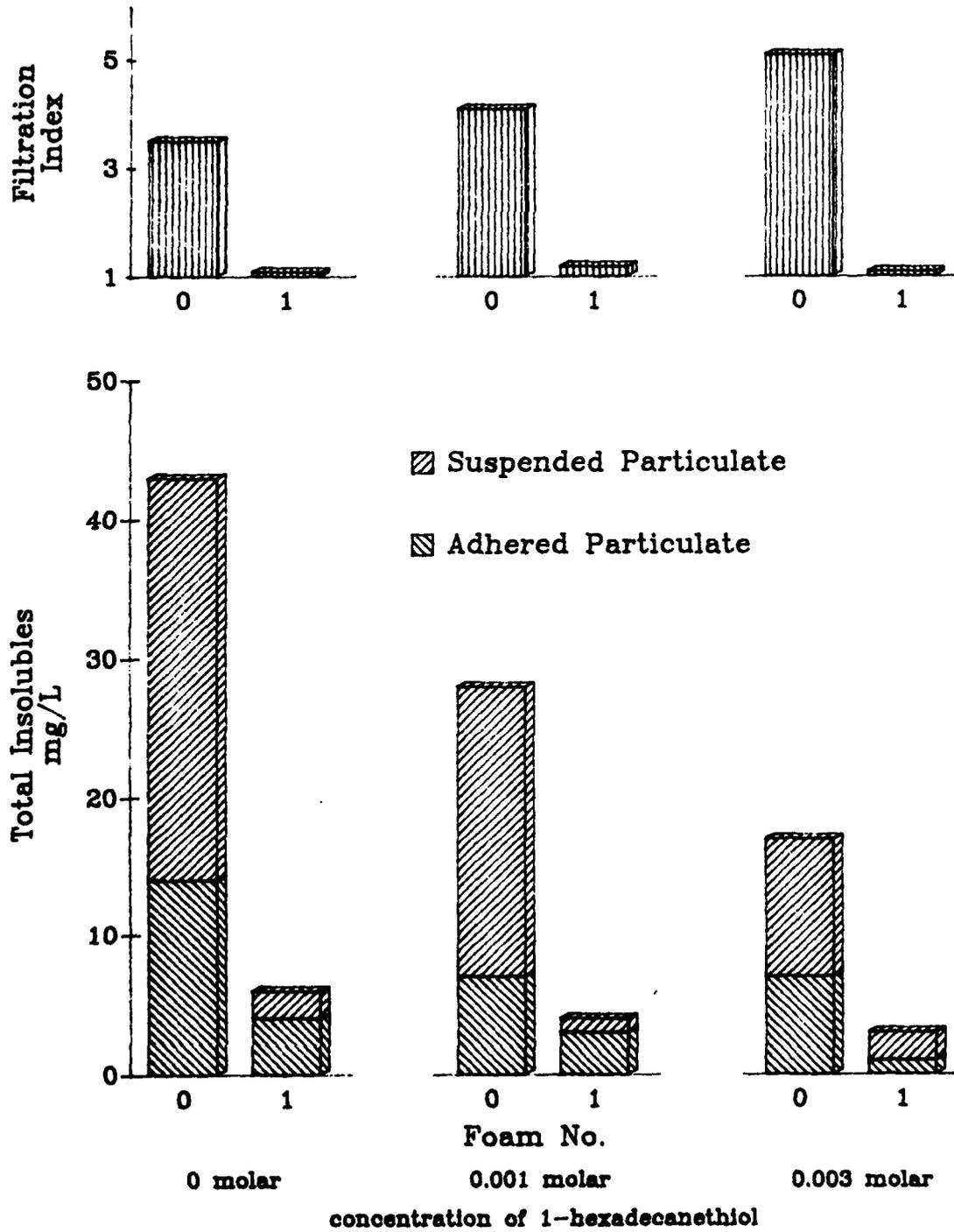
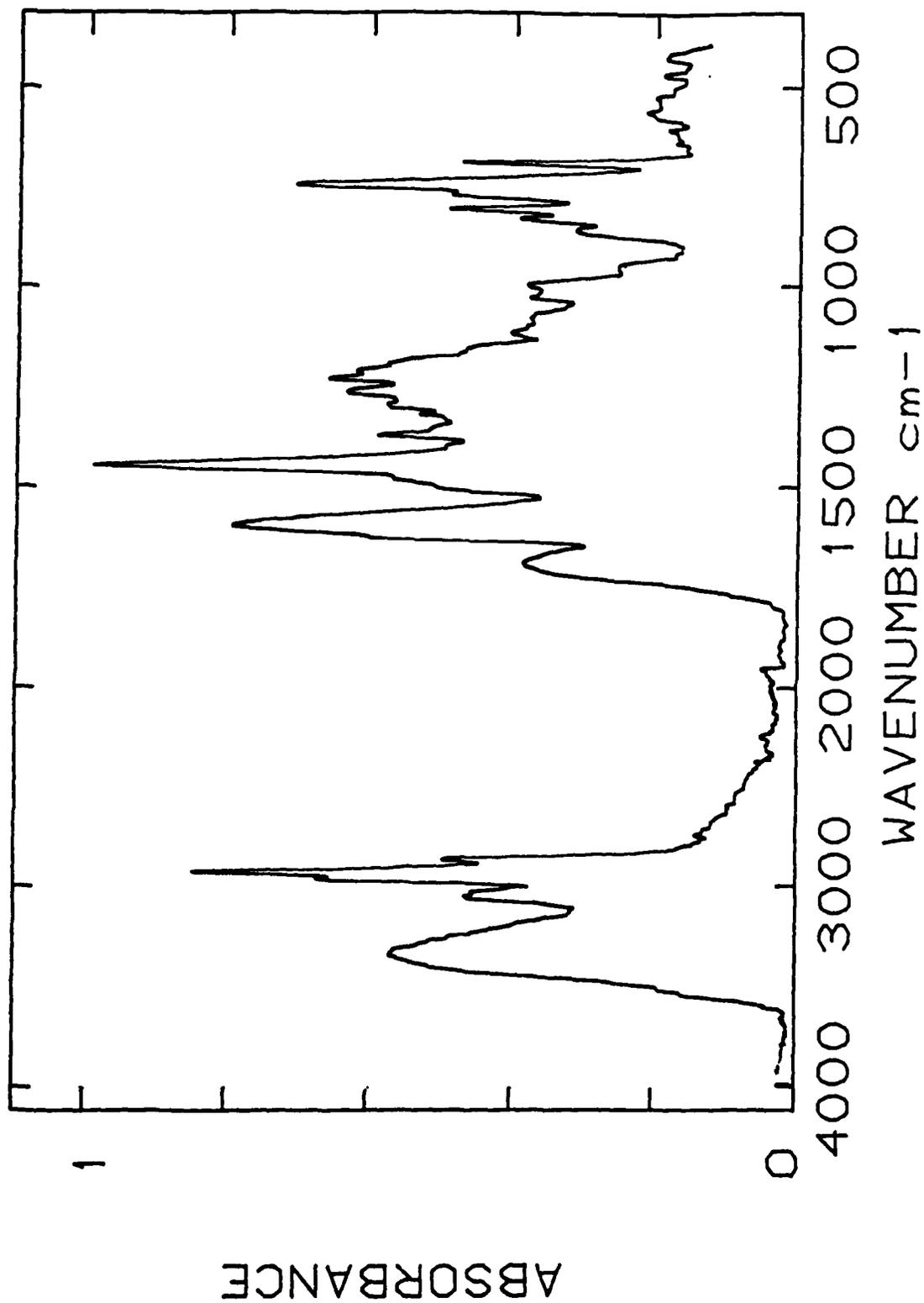


FIGURE 9  
Infrared Spectrum of Methylene Chloride  
Extract from Aged FSF 13



## APPENDICES

Appendices A-F contain the experimental data on which this report is based. Values for total insolubles and particulate matter are presented. Adherent gum may be read as the difference between those values. The initial colour (by ASTM D1500) of the 30:70/LCO:SRD fuel blend was 1.5. All samples were run in duplicate. Filtration Index values were calculated from average filtration time (sec) for duplicate 100 ml aged fuel samples, divided by 90 sec filtration time for fresh 100 ml fuel sample.

### Summary of Appendices:

<b>APPENDIX</b>	<b>FUEL STABILITY MODIFICATION SYSTEM</b>
<b>A</b>	<b>Fuel/PU Foam</b>
<b>B</b>	<b>Fuel/PU Foam Fuel/FOA-3 and FOA-15</b>
<b>C</b>	<b>Fuel/PU Foam/BENZENETHIOL Fuel/PU Foam/CHLOROACETIC ACID Fuel/PU Foam/n-HEXADECATHIOL</b>
<b>D</b>	<b>Fuel/PU Foam/COPPER NAPHTHENATE</b>
<b>E</b>	<b>Fuel/PU Foam PRE-TREATMENT</b>
<b>F</b>	<b>Multiple Use of PU Foam Samples</b>

## APPENDIX A

### Fuel/PU Foam

PU Foam No. (see Table 2)	PU Foam Weight (g/L)	Total Insolubles (mg/L)	Particulate Matter (mg/L)	Filtration Index	PU Foam WT Increase (mg/L)	ASTM D1500 Colour (Final)
<b>Fuel Ageing: 43°C - 26 weeks</b>						
-	-	49	13	1.6	-	4.5
#1	1.90	11	7	1.2	48	4.0
#2	6.35	3	0	0.9	140	3.5
#8	2.75	1	1	1.1	N.D.	4.0
#9	3.65	3	0	1.0	N.D.	4.0
#10	3.70	2	0	1.1	141	4.0
#11	3.95	0	0	1.0	130	4.0
#12	3.10	3	1	1.1	109	4.0
#13	2.65	3	3	1.2	90	3.5
<b>Fuel Ageing: 80°C - 7 days</b>						
-	-	55	44	2.8	-	5.5
#3	6.64	10	7	3.5	133	4.5
#4	4.70	14	6	3.7	94	4.0
#5	5.88	25	15	5.0	*	5.0
#6	7.25	13	7	4.5	174	4.0
#7	7.93	11	3	3.9	119	4.0

N.D. - not determined

\* - incomplete removal of residual fuel from foam

**APPENDIX B**

**Fuel/PU Foam/FOA Fuel Additives**

Fuel Additive	Additive Amt:(g/L) or [ppm]	Total Insolubles (mg/L)	Particulate Matter (mg/L)	Filtration Index	PU Foam WT Increase (mg/L)	Colour (Final)
<b>Fuel Ageing: 80°C - 13 days</b>						
-	-	45	39	2.8	-	4.5
Foam #1	(2.27)	8	4	1.5	70	4.0
Foam #2	(9.92)	4	3	1.2	179	3.0
FOA-15	[24]	10	2	1.9	-	5.5
FOA-3	[24]	21	5	3.6	-	4.5
<b>Fuel Ageing: 120°C - 72 hours</b>						
-	-	128	100	3.6	-	5.0
Foam #1	(6.57)	17	8	1.6	0	3.5
Foam #2	(9.29)	14	6	2.1	204	3.5
FOA-3	[24]	61	9	3.5	-	4.0
<b>Fuel Ageing: 120°C - 96 hours</b>						
-	-	182	140	3.4	-	5.5
Foam #1	(6.33)	97	82	1.8	net loss	4.0
Foam #2	(9.30)	38	10	2.2	335	3.5

## APPENDIX C

### Fuel Additives

Fuel Ageing: 65°C - 43 days

Foam #1 Amount (g/L)	Additive (mol/L)	Total Insolubles (mg/L)	Particulate Matter (mg/L)	Filtration Index	Foam WT Increase (mg/L)	Colour (Final)
<b>Benzenethiol</b>						
-	-	43	29	3.5	-	4.5
(2.58)	-	6	2	1.1	72	4.0
-	[0.001]	217	1	1.1	-	5.0
(2.66)	[0.001]	2	2	1.1	194	4.0
-	[0.003]	600	0	1.3	-	6.0
(2.84)	[0.003]	9	2	1.3	349	5.5
<b>Chloroacetic Acid</b>						
-	[0.001]	104	67	2.6	-	5.5
(3.54)	[0.001]	9	4	1.1	152	5.0
-	[0.003]	154	121	2.6	-	6.0
(3.54)	[0.003]	29	18	1.8	156	5.5
<b>1-Hexadecane-thiol</b>						
-	[0.001]	28	21	4.1	-	7.0
(3.66)	[0.001]	4	1	1.2	55	4.5
-	[0.003]	17	10	5.1	-	7.0
(3.69)	[0.003]	3	2	1.1	59	4.0

## APPENDIX D

### Fuel Additive

Foam #1 Amount (g/L)	Copper Naph- thenate Conc. (mg/L)	Total Insolubles (mg/L)	Particulate Matter (mg/L)	Filtration Index	Foam WT Increase (mg/L)	Colour (Final)
Fuel Ageing: 80°C - 13 days						
-	-	39	35	2.4	-	4.5
(2.27)	-	8	4	1.6	70	4.0
-	[0.25]	70	54	2.2	-	5.0
(2.59)	[0.25]	8	7	1.3	132	5.0
-	[1.00]	67	58	2.8	-	5.5
(2.67)	[1.00]	13	9	1.3	158	6.0

## APPENDIX E

### Fuel/PU Foam Pretreatment

1st Foam in Fuel Immersion (Foam #1)	2nd Foam in Fuel Immersion (Foam #1)	Total Insolubles (mg/L)	Filtration Index	Colour (Final)
Fuel Ageing (Foam #1 Absent) - 80°C - 14 days				
-	-	39	3.4	4.5
5 days/room temp.	-	37	2.9	4.5
5 days/room temp.	3 hours/120°C	23	4.0	4.0
5 days/room temp.	7 hours/120°C	15	2.9	4.0
3 hours/120°C	-	39	2.5	4.5
7 hours/120°C	-	46	2.9	4.5

## APPENDIX F

### Multiple Use of PU Foam Samples

PU Foam No.	PU Foam Weight (g/L)	Total Insolubles (mg/L)	Particulate Matter (mg/L)	Filtration Index	PU WT Increase (mg/L)	ASTM D1500 Colour (Final)
<b>Fuel Ageing: 120°C - 3 days</b>						
<b>Run No. 1:</b>						
-	-	127	106	2.3	-	5.0
#1	4.84	24	12	1.4	238	3.0
#2	6.78	19	10	1.6	362	3.0
<b>Run No. 2:</b>						
-	-	129	87	3.6	-	5.0
#1	5.05	16	8	1.4	264	3.5
#2	7.14	14	6	1.7	251	3.5
<b>Fuel Ageing: 120°C - 4 days</b>						
<b>Run No. 3:</b>						
-	-	177	140	3.4	-	5.5
#1	5.01	51	25*	1.8	net loss	4.0
#2	7.39	38	11	2.2	335	3.5

\* PU foam cells on filter membrane

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## ABSTRACT

A new means of increasing the chemical stability of petroleum fuel during storage has been developed. Distillate fuel blends have been shown to form significantly less total particulate matter (comprising the sum of the suspended insoluble and adhered particulate matter) following storage in contact with Fuel Stability Foam (FSF) than similar reference fuels aged in the absence of FSF. The most effective FSF material has been found to be a reticulated polyurethane which maximizes the fuel stabilizing properties. This effect is at least equivalent to that of any known fuel-soluble chemical stabilization additive. Enhanced filterability and decreased colouration of fuels after storage in contact with FSF were also observed. Total insolubles in aged fuels containing known deposit promoting agents, including carboxylic acids, soluble copper and aromatic thiols, were reduced to low levels by the presence of FSF. Contributing mechanisms for the stabilizing action of FSF include adsorption by the FSF of chemical precursors to the particulate matter, adsorption of soluble particulate matter, solution of solid particulate matter in the foam and adsorption and interaction with species to modify the acid/base environment of the fuel. The advantages of using FSF for fuel stabilization in both military and non-military fuel systems are considered.