QUANTITATIVE DETERMINATION OF CORROSION INHIBITORS IN MIDDLE DISTILLATE JET FUELS BY GEL PERMEATION CHROMATOGRAPHY

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SUMMARY

A method which efficiently extracts commercial corrosion inhibitors from aircraft turbine fuels and qualitatively and quantitatively determines them by gel permeation chromatography is described. Additive concentration for quantitation ranges between 1 and 35 ppm (v/v). In addition the fate of the corrosion inhibitors at these concentrations in fuel was examined in the presence of steel surfaces, fresh water and seawater.

INTRODUCTION

Corrosion inhibitors are mandatory additives for U.S. Navy jet fuels[1]. They are added to reduce corrosion in storage tanks, transfer lines and other fuel handling equipment and hardware. Moreover, they are known to enhance lubricity properties of hydro-treated fuels[2–4].

It is known that, as fuels pass through transfer lines or are stored, the level of corrosion inhibitor present decreases and with this decrease there is a corresponding decrease in both the corrosion protection and the lubricity of the fuel[2–4]. Under extreme cases this loss of corrosion inhibitor can cause fuel pump failure. Thus, an analytical method was sought to quantitatively determine the concentration of corrosion inhibitors in fuel samples so that levels could be monitored with time and appropriate adjustments to additive concentration could be made. The major thrust of this work was the development of a sensitive analytical method for quantifying corrosion inhibitors in fuel. A secondary goal was to gain more specific experimental evidence regarding the fate of the inhibitors.

Commercially available corrosion inhibitors (currently approved for U.S. Naval use)[1] are typically combinations of a fatty acid dimer, a substance which has a molecular weight approximately one-half that of the dimer, and other, lower molecular weight species such as ethylbenzene and naphthalenes (serving as a solvent for

the active ingredients). A typical dimer used is dilinoleic acid, which is considered to be the active ingredient in many of the corrosion inhibitors[5].

The method described in this work used a solvent extraction procedure for removing the corrosion inhibitor from the fuel followed by gel permeation chromatography (GPC). Because the typical additive concentration in fuel is less than 35 ppm (w/v), the concentration range studied was 2–30 ppm. Nine military approved corrosion inhibitors were selected for GPC analysis and two of these were used to develop and test the method and for other experimental work. Results indicate that 100% of the active ingredient can be recovered by extraction and quantitation then effected by GPC. The active ingredient is usually eluted from a 50-Å Microspherogel column within 6 min after injection.

EXPERIMENTAL

Equipment

Samples were subjected to GPC analysis on a system which used a modular Spectra-Physics pump system with a Waters Model 401 differential refractive index detector. The pump system utilized a Model 740 dual-piston reciprocating pump, a Model 740-C pump control and a Model 714 pressure monitor. Samples were injected into a Rheodyne Model 7125 loop/valve type injector. Chromatograms were recorded using either a Varian Model 9176-07 or a Fisher Recordall Series 5000, Model D5117/5AQ strip chart recorder. Peak integration was performed using a Hewlett-Packard Model 3390-A integrator. The column used for much of the work was a Beckman-Altex Microspherogel column, Model 255-80 (50 Å pore size, 30 cm × 8.0 mm I.D.). Fisher HPLC grade uninhibited tetrahydrofuran (THF) was used as the mobile phase.

TABLE I

QUALITATIVE GPC ANALYSIS OF APPROVED MILITARY SPECIFICATION CORROSION IN-HIBITORS

Additive	Manufacturer	Retention volume (ml)[*]	
		Peak 1	Peak 2
DCI-4A	E. I. DuPont de Nemours & Co. (Deepwater, NJ, U.S.A.)	6.0	6.9[**]
Nalco 5403	Nalco Chemical Co. (Sugar Land, TX, U.S.A.)	6.0	6.5
Nalco 5405	Nalco Chemical Co. (Sugar Land, TX, U.S.A.)	6.0	6.5
Hitec 580	Edwin Cooper, Inc. (Saugent, IL, U.S.A.)	5.8	6.3
Tolad 245	Petrolite Corp. (St. Louis, MO, U.S.A.)	6.0	6.4
Tolad 249	Petrolite Corp. (St. Louis, MO, U.S.A.)	6.0	6.6
Unicor J	Universal Oil Products (McCook, IL, U.S.A.)	5.9	—[***]
Mobilad F-800	Mobil Chemical Co. (Edison, NJ, U.S.A.)	5.9	6.8
Lubrizol 541	Lubrizol Corp. (Painsville, OH, U.S.A.)	5.9	6.4

   [*] Data taken from Figs. 1–5; peaks are in order of elution.
  [**] Well-resolved peak.
 [***] Not detected.

Method

Nine corrosion inhibitors were selected for study. They are listed in Table I. Samples of each were dissolved in THF to concentrations of 1000 ppm (v/v) and subsequently injected onto a GPC column for separation. While preliminary work was done with a 100-Å Microspherogel column (Beckman-Altex Model 255-81) it was found that slightly better separation could be achieved with the 50-Å column. Therefore, that column was used for most of the work. The usual injection volumes were 80 or 100 μl and flow-rates were approximately 1 ml/min. Following initial GPC screening of the nine additives, two were selected for further investigation: Unicor J and Mobilad F-800. They were extracted from fuels using a method which is somewhat similar to that used by Hillman *et al.*[5]. There are, however, differences in the relative volumes of the extractions used and in the extractants themselves.

Our extraction method uses a volume of jet fuel extracted with an equal volume of 0.2 M sodium hydroxide. For low concentrations of inhibitor we use 250 ml of jet fuel and 250 ml of aqueous base. The two phases are shaken well together and allowed to separate. The aqueous phase is then drawn off and acidified with concentrated hydrochloric acid to pH 2, which is well below the pK_a for the organic acids. After acidification the aqueous phase is back extracted with an equal volume of methylene chloride and allowed to evaporate to dryness at ambient temperature. The material left in the beaker after evaporation is dissolved in small portions of THF, the inside of the beaker is rinsed well and the dissolved material is collected in a corner of the beaker. It is eventually taken up in exactly 5.0 ml of THF and transferred to a glass vial with a PTFE cap liner.

For much of this work, commercial aircraft fuel, Jet A, which is a middle distillate kerosene based fuel[6] was used. Jet A was chosen because it is similar to JP-5 and contains no mandatory additives. Samples of Jet A were spiked with known quantities of the selected additives to make solutions which had known concentrations of corrosion inhibitors in jet fuels. To prepare samples for extraction and subsequent GPC analysis, corrosion inhibitors were added to the Jet A by syringe and the fuel was then shaken well to dissolve the corrosion inhibitor. Samples prepared to test the method were made up in the concentration range 2–30 ppm (v/v). Density determinations were made for each of the additives. In general, the densities were in the range 0.92–0.94 g/ml. Thus, a sample which was 10 ppm (v/v) would be approximately 9.2 ppm (w/v). Analytical data were obtained through the use of comparator standards. These were prepared by dissolving calculated volumes of corrosion inhibitors in appropriate volumes of THF to match the concentration of the extracted sample. For example: a 250-ml jet fuel sample spiked to contain 20 ppm of Unicor J (v/v) would yield 5 ml of a 1000-ppm solution after extraction and dissolution in 5 ml of THF. The comparator standard would be a 1000-ppm solution of Unicor J in THF. In general, comparators were made the same day as the GPC analyses.

Following their preparation, samples and standards were injected onto the column. A 200-μl maximum capacity injection loop was used. Experiments were performed to test the linearity of recorder/integrator response as functions of sample concentration and injection volume. Both were linear over the ranges of interest. GPC experimental parameters are summarized as follows: flow-rate, 1 ml/min; recorder range, 10 mV; recorder chart speed, 0.5 cm/min; integrator time constant, 0.64 ms; integration threshold, 2 exp 4; detector span, ×4; temperature, ambient; injection volume, 80–100 μl; and solvent/mobile phase, THF.
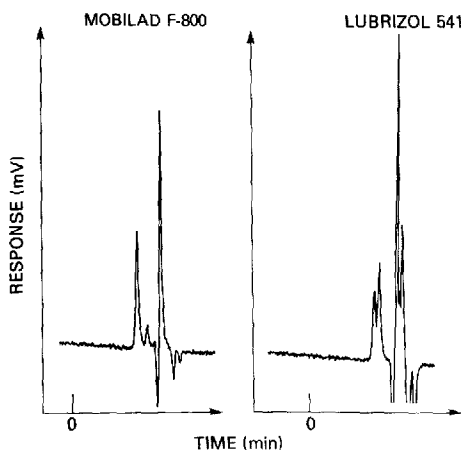
Fig. 1. Typical gel permeation chromatograms of Mobilad F-800 and Lubrizol 541 dissolved in THF (1000 ppm, w/w). RI detector, THF flow-rate of 1 ml/min.

Peak area information was obtained through the use of an electronic integrator; Peak heights were generally taken from the strip chart recording.

RESULTS AND DISCUSSION

Figs. 1–5 are representative chromatograms obtained for the nine corrosion inhibitors available for study. These were obtained using a single 50-Å column. Chromatograms are read from left to right; the heaviest (left most peak) component corresponds to the fatty acid dimer. It can be seen that there are distinct similarities and differences between the graphical GPC data of the nine inhibitors. Each chromatogram exhibits a peak that corresponds with a substance of molecular weight greater than 500 —the dimer. This peak, in each case, has a retention volume of approximately 6 ml (3 cm from the injection point). Each chromatogram also exhibits one or more large peaks which begin with an elution volume of 8 ml (4 cm). These peaks represent substances of much lower molecular weight, such as ethylbenzene and naphthalenes, which act as a solvent system for the active ingredients. It can be seen
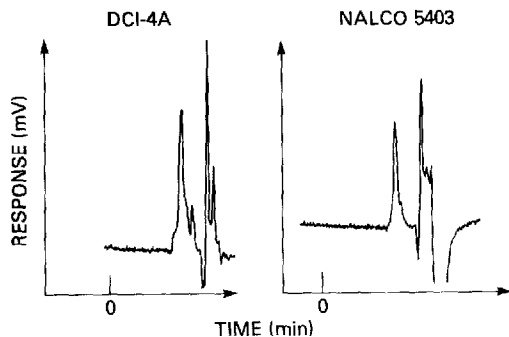

Fig. 2. Typical gel permeation chromatograms of DCI-4A and Nalco 5403 dissolved in THF (1000 ppm, w/w). RI detector, THF flow-rate of 1 ml/min.
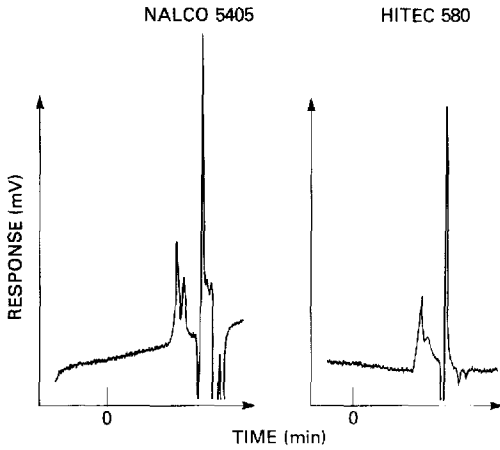
Fig. 3. Typical gel permeation chromatograms of Nalco 5405 and Hitec 580 dissolved in THF (1000 ppm, w/w). RI detector, THF flow-rate of 1 ml/min.

that the ratio of the first (largest) of these low molecular weight peaks and the fatty acid peak varies considerably from additive to additive. A major difference, other than the peak ratios, to be observed in each chromatogram is a second peak, possibly an acid phosphate ester[7] which follows the fatty acid peak in all GPC traces except that of Unicor J. In some cases (Nalco 5403, Hitec 580) it appears as a poorly resolved shoulder on the trailing side of the dimer peak. Elsewhere it appears to be a well-resolved peak; in some cases it is more intense than the fatty acid peak. While the
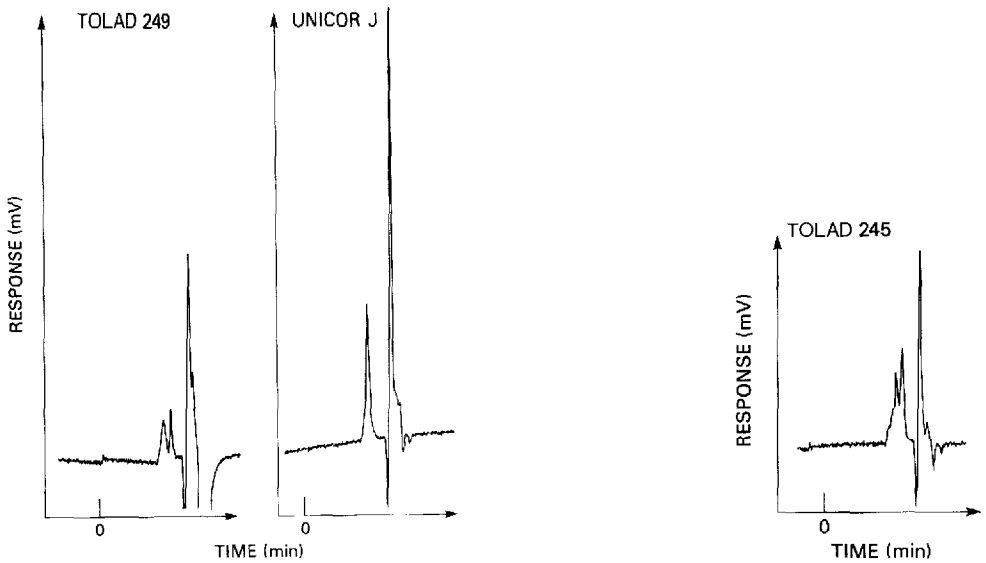

Fig. 4. Typical gel permeation chromatograms of Tolad 249 and Unicor J dissolved in THF (1000 ppm, w/w). RI detector, THF flow-rate of 1 ml/min.

Fig. 5. Typical gel permeation chromatogram of Tolad 245 dissolved in THF. RI detector, THF flow-rate of 1 ml/min.

retention volume is about 0.5 ml greater than that of the dimer (Table I) there are two exceptions: DCI-4A and Mobilad F-800 show 0.9-ml differences between the first and second resolved peaks. The DuPont additive, however, also has a shoulder on the trailing edge of peak 1, the retention volume of which could resemble peak 2 in most of the other additives.

Of particular note is the relative intensity of the dimer peak from additive to additive for constant (1000 ppm, v/v) concentrations. There is as much as a three-fold difference in peak height (compare Unicor J with Tolad 249) for similar concentrations. A change to w/v calculations would make little difference because of similarities in the calculated densities of the additives. The peak height, and thus peak area differences could make quantitation difficult unless it is known which specific additive has been added to a particular fuel or unless the chromatograms could identify qualitatively specific additives. However, it is fairly obvious that in the absence of interfering species different additives can be specifically identified on the basis of their GPC fingerprints.

Initial work performed on the development of the extraction method used dissimilar volumes of fuel and aqueous base followed by the acidified aqueous phase/methylene chloride extraction. There were typically three extractions performed in each phase of the process and the volumes were combined. The extraction efficiency for samples extracted in this manner was found to be no better than 88% as determined by GPC analysis and comparison of peak heights and areas with comparators. Parameters such as pH of the aqueous phase and recovery of the additive after evaporation of the methylene chloride phase were adjusted with varying results. However, none yielded 100% recovery of the additive.

Series of extractions were performed to determine optimal extraction volume parameters. Each extraction involved 250 ml of Jet A spiked with 50 ppm (v/v) of Mobilad F-800. Results are shown in Table II. For the first set of extractions, the volume of aqueous phase was varied and the volume of methylene chloride used to perform each back extraction was equal to the volume of aqueous phase used. Thus, the Jet A sample extracted with 175 ml of aqueous base used a back extraction volume of 175 ml. A second and third series of extractions which used extraction volumes of aqueous and organic phases equal to those used in the first series were also run on the same Jet A samples. GPC analysis of these fractions indicated that extraction was complete for the 250 ml/250 ml system after the first extraction, whereas second and third series extractions on the 250 ml/175 ml and 250 ml/100 ml systems yielded detectable quantities of Mobilad F-800. For the second set of extractions the volume of aqueous base used was held constant at 250 ml and the volume of methylene chloride used to back extract the samples was varied. It can be seen, from Table II, that extraction with equal volumes of fuel/aqueous base followed by a back extraction which uses the same volume parameters provides optimum efficiency.

Only one extraction series was performed on the second set of samples. Quantitation was accomplished by comparing areas of the sample peaks with that of a comparator made to have the same concentration in THF as the theoretical concentration of an extracted sample of 50 ppm Mobilad F-800. It can be seen that extraction efficiency is optimized when the volumes of extracting solutions, whether for the direct or back extraction, are equal to that of the jet fuel. For those extractions all the Mobilad F-800 added to the fuel was recovered.

TABLE II

RESULTS OF EXTRACTION SERIES PERFORMED TO DETERMINE OPTIMUM EXTRAC-
TION VOLUME PARAMETERS USING MOBILAD F-800

Average area of comparator standard peak (integrator counts) = $3.92 \pm 0.05 \times 10^{5*}$.

Sample, extraction series	$V_{NaOH}/V_{CH_2Cl_2}$	Area of dimer peak (integrator counts $\times 10^5$)*	Extraction efficiency (%)
1	250 ml/250 ml	4.01	102
1	175 ml/175 ml	3.62	92
1	100 ml/100 ml	3.35	85
2	250 ml/250 ml	4.07	103
2	250 ml/175 ml	3.62	92
2	250 ml/100 ml	3.55	90

* Four injections were made.

To test the method, 250-ml samples of Jet A were spiked with enough Mobilad F-800 to make samples which were 5, 10, 15, 20 and 30 ppm (v/v) in the additive. Each sample was then extracted with one 250-ml volume of aqueous base and re-extracted with one 250-ml volume of methylene chloride following acidification of the aqueous phase. After extraction the additive was recovered as previously described and then taken up in 5.0 ml of THF. Comparator standards were made by dissolving the same quantity of additive as had been used to spike the jet fuel samples in 5.0 ml portions of THF. One comparator was made for each spiked sample. The same procedure was used for an identical series in which the additive used was Unicor J. Figs. 6 and 7 are plots of GPC peak area *versus* concentration for the Mobilad F-800 and Unicor J series respectively. Both plots include points for the extracted and standard (comparator) samples. It is obvious from the data obtained and plotted that the sample and standard curves coincide exactly, attesting to the efficiency of the method.
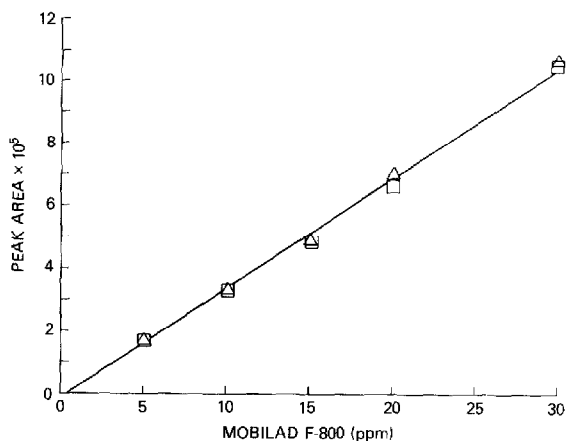

Fig. 6. Plot of extracted and standard concentrations of Mobilad F-800 *versus* peak area of active ingredients. □ = standard samples; △ = extracted samples.
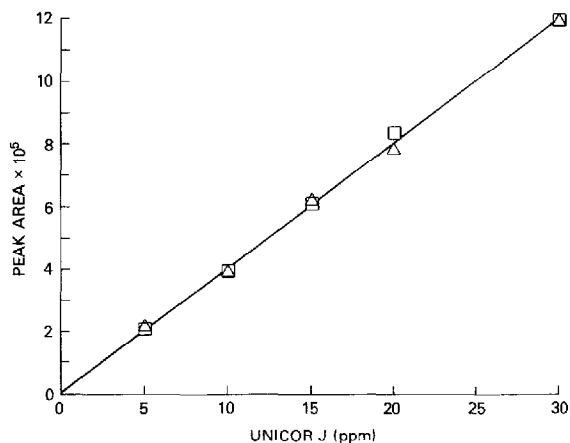
Fig. 7. Plot of extracted and standard concentrations of Unicor J *versus* peak area of active ingredients. □ = Standard samples; △ = extracted samples.
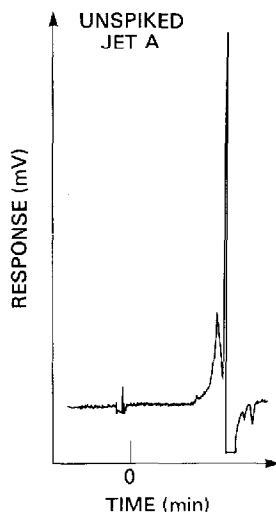
Fig. 8. Typical gel permeation chromatogram of additive-free Jet A after extraction. Detector and flow conditions as in Figs. 1–5.

Our work indicates that attaining concentration levels of 2 ppm or less is feasible. However, there are some difficulties in quantitative analysis. This derives largely from the fact that there are components of the jet fuel itself which extract into the aqueous base and are carried over into the final sample along with the corrosion inhibitor. Fig. 8 is a gel permeation chromatogram of a sample of additive-free Jet A which has been carried through the extraction process. The first peak appears at a retention volume of approximately 6.8 ml and can interfere with or mask a low intensity additive peak. Samples of additive-free JP-5 extracted similarly have similar chromatograms. Thus, in order to obtain meaningful quantitative results at that level, the fuel component should be excluded. However, low concentrations (less than 2 ppm) can be semi-quantitatively determined by estimating the height of the additive peak which appears as a shoulder on the leading edge of the fuel component peak. It should be noted that the concentration of the active ingredient of interest (the fatty acid) determined by this method is considerably less than that of the total inhibitor concentration which is expressed as ppm (v/v) because the concentration of fatty acid in the commercial additive packages is on the order of 40% (v/v)[2].

DETERMINATION OF THE FATE OF CORROSION INHIBITORS

Experimental

Two experiments were performed to examine the loss of corrosion inhibitors from fuels during storage/transfer operations. One tested the "plating-out" theory[2,3], *i.e.*, that the inhibitor tends to plate-out on the metal surfaces of transfer lines and storage tanks. A second experiment was performed to determine whether there is an ionic complexing effect when the fuel, and hence the inhibitor, is in contact with

seawater. The plating-out experiments measured inhibitor loss as functions of time and metal surface area. In experimental set A, extractions were performed on a group of six 250-ml samples of a JP-5 fuel (NRL No. 85-12) containing about 5 mg of corrosion inhibitor. Each sample had been in contact with a constant weight (approximately 19 g/sample) and hence a relatively constant surface area (estimated surface area of 400 cm²), of clean stainless-steel wool. A control sample, with no steel wool present was also run (glass beaker surface area about 210 cm²). Samples were subjected to varying periods of contact time with the steel wool. For experimental set B, Jet A was used as the fuel and the mass of steel wool (and thus the surface area) was varied and time was held constant. All samples removed for extraction were 250 ml and additive (Mobilad F-800) concentrations were 20 ppm (v/v). Extraction and GPC procedures used were the same as those described above.

The ion complex effect was tested as follows: a 750 ml sample of Jet A was spiked with 15 μl of Mobilad F-800 to yield a solution with an additive concentration of 20 ppm (v/v). A 250-ml aliquot (sample 1) was removed and placed in a clean bottle and stored away from light for 16 days. A second 250-ml aliquot (sample 2) was removed and placed in a bottle which contained 250 ml of synthetic seawater[8] and subjected to the same storage conditions. Both bottles were occasionally gently agitated, but not shaken, to simulate the rolling motion of a ship. Finally the last aliquot (sample 3) was immediately extracted with seawater. After the 16 day storage period, sample 1 was extracted with aqueous base and the seawater layer from sample 2 was separated from the fuel. The aqueous layer, whether seawater or base, from each sample was acidified to pH 2 and the usual procedure for back-extraction and GPC analysis was followed. In a later experiment, spiked fuel samples were exposed to distilled water rather than seawater to test the "salting-out" effect.

RESULTS AND DISCUSSION

Effect of metal surfaces

Table III summarizes the results of the time/concentration and surface area/concentration studies. For the time/concentration studies it appears that there is no significant concentration decrease over the long term. It is probable that there is an

TABLE III

RESULTS OF "PLATING-OUT" EXPERIMENTS

Time/concentration study			*Surface area/concentration study*		
Sample	Exposure time (h)	Additive recovered (%)	Sample	Steel wool (g)	Additive recovered (%)
1	1.5	72.5	1	7.5	83.5
2	3.0	72.8	2	15.0	73.8
3	20	74.1	3	22.5	73.8
4	93	58.1	4	30.0	71.6
5	168	83.3			
6	282	81.0			
7 (Control)	282	88.6			

almost immediate plating out (1.5 h) followed by a period of relatively little activity. There are differences in the percent recovery data between the first 3 and last 3 samples. However, an average of all 6 results yields 73.7% recovery. The control sample (No.7) was treated the same way as samples 1–6 with the exception that there was no steel wool present in the beaker used to age the samples. It is likely that incomplete recovery of the additive is caused by adsorption (plating-out) of the inhibitor on the glass surface. At the 5 mg level of acid dimer estimated in these samples, a monolayer surface area of coverage would be about 2000 cm². This means about 11% of the acid dimer would be expected to plate out on the beaker walls and an additional 20% would plate out on the steel wool surface.

For the surface area/concentration studies, the data are in substantial agreement with those obtained in the time/concentration study. It is possible that one would need more precise control of the surface area than that provided by steel wool to show precise differences in the concentration of additive recovered. In any case, this work seems to indicate that surface adsorption plays a definite part in additive "loss" on clean surfaces. Additional experiments using other surfaces are currently underway.

Effect of seawater

The seawater experiments yielded truly interesting results. Sample 1, the control sample, was extracted with aqueous base after the 16 day storage and analyzed, using freshly prepared comparators, for Mobilad F-800. The recovery was found to be 83.2% which is fairly consistent with results obtained from the previous set of experiments for additive adsorption (plating-out) on inside surfaces of storage containers.

Sample 2, which was stored over seawater, was extracted with base and analyzed using our method. No additive was recovered. The seawater layer was acidified, back-extracted and subjected to GPC analysis with identical results. An amber-colored solid was observed to form at the interface between the fuel and seawater. This insoluble material was isolated from the system. It was dissolved in acid to pH 2, extracted with methylene chloride and analyzed. While the results were not quantitated, GPC analysis yielded a substantial additive peak. There is about 375 mg of Ca^{2+} and Mg^{2+} available in 250 ml of seawater. This is more than adequate to effect an insolute interfacial salt formation with the 5 mg of dimer acid in 250 ml of fuel.

Sample 3 was immediately extracted (no storage period) with seawater and then subjected to the same procedure as was applied to sample 2. Exactly the same results were obtained *i.e.*, that the additive was found only in the interfacial material. The obvious implication from these experiments is that there is salt formation between the additive and the group II metal ions (Ca^{2+} and Mg^{2+}) and that the soap formed is insoluble in both liquids. Thus, seawater intrusion into fuel storage tanks would be likely to remove any corrosion inhibitors present.

A series of experiments which substituted fresh (distilled) water for seawater produced no interfacial material and no water extractable material. Thus it can be concluded that water itself is not involved in the reduction of additive concentration.

CONCLUSIONS

A method has been established for quantifying corrosion inhibitor levels in Navy jet fuels and 100% recovery of the additive from fuel is possible. Concentrations of 5 ppm (v/v) are easily determined and the detection and determination of as little as 1–2 ppm is possible. It was possible to qualitatively distinguish nine commercially available corrosion inhibitors at the 1–2 ppm level.

Results obtained from studies dealing with the fate of the corrosion inhibitors are interesting and indicate that seawater, in particular, effectively removes the corrosion inhibitor from fuel. The need to expand this work to include more studies on the "plating-out" or adsorption phenomena is indicated.

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