Identification of the Active Corrosion Inhibitors in Nitrated Mineral Oils

D.A. Al-Sammerrai, Q.S. Majeed and W.D. Saleem

Petroleum Research Centre, P.O. Box 10039, Jadiriyah, Baghdad, Iraq.

ABSTRACT. Nitration of aromatic hydrocarbons in mineral oils with dilute nitric acid at 50°C depends on the number of rings. Under these conditions the mono- and di-nuclear aromatics were not susceptible to nitration, while the tri-aromatics were easily converted to the nitrated products. The anti-corrosion properties of nitrated mineral oils is attributed to the presence of these products.

One of the most highly effective methods for producing oil soluble corrosion inhibitors is the process of direct nitration of mineral oils with nitric acid (Dolberg *et al.* 1964). The nitrated oils, thus obtained after washing off the acid with alkali are good corrosion inhibitors (Reshetnikov 1970). The best protective properties are shown by the products obtained by nitrating oils with average molecular weight of about 400. Such inhibitors are only miscible with non-aqueous media and may be used either independently or as anti-corrosion additives for oils, greases, fuels, etc. (Reshetnikov 1972).

Recently, nitrated oil possesing good anti-corrosion properties was obtained from base stock mineral oil derived from Kirkuk crudes (Al-Sammerrai and Ahmed 1980). Only the aromatic constituents of the mineral oil are susceptible to electrophilic substitution under the mild conditions of the acid treatment (Finar 1973).

Since it has not been established which type of aromatic constituents are contributing to corrosion inhibition, it would be of practical and scientific importance to investigate the active corrosion inhibitor in the nitrated product.

Experimental

Paraffinic and aromatic components of the base mineral oil were separated using adsorption chromatography on a column packed with silica gel. Different cuts were identified according to their refractive indices which is related to the ring size of the aromatic hydrocarbons (Dovgopolyi and Eminov 1968).

Attempted nitration of mono-, di- and tri-nuclear hydrocarbons was performed by dissolving a known concentration of each fraction in the paraffinic cut of the oil, followed by treatment with 50% nitric acid at 50°C for 4 hr with continuous stirring. The oil was separated, neutralised, washed well with water, and then heated to 110°C to drive off moisture; this was followed by filtration.

Elemental analysis, infrared and nuclear magnetic resonance spectroscopy were used as tools in the assessment of the relative chemical composition of the products obtained.

Evaluation of the corrosion inhibition of the aromatic fractions as well as the original nitrated oil was assessed to standard procedure (Ranney and Al-Sammerrai 1973). This involved measuring the weight loss of a standard copper plate immersed in an oil to which was added the above products in different concentrations. The oil was heated to $140 \pm 1°C$. An air flow through the oil was maintained at such a rate as te keep 2/3 of the bulk in the foaming state ($\sim 5l$/min). This would be enough for the complete immersion of the metal plate. The degree of inhibition of corrosion was assessed by measuring the differences in weight of the copper plate before and after 6 hr of immersion in the hot foaming oils. Units of weight loss were expressed in milligrams per square decimeter per day. The increase in the acid number at the end of the experiment was also recorded.

Results and Discussion

Separation of the base oil having an average molecular weight 420 and a viscosity of 11.5 cSt at 98.9°C was achieved by employing selective adsorption chromatography on a silica gel column. Table 1 shows the percentage concentration by weight of different fractions and their corresponding refractive indices.

A blend of each aromatic fraction in the paraffinic cut (10% concentration by weight) was prepared and subjected to nitration under the conditions described earlier.

Infrared spectra using a Pye Unicam SP3-300 instrument of the nitrated oil and tri-aromatic fractions showed a weak absorption at 1530 and 1320 cm^{-1} due to NO_2 streching vibrations. No NO_2 absorption was detected in the ir spectra of the other two products.

Table 1. The percentage concentration by weight of different fractions obtained and their corresponding refractive indices.

Type of cut	R.I. at 20°C	Accepted range*	% by wt.
Base oil	1.48623	—	—
Paraffins	1.47785	< 1.49	90.5
Mono-aromatics	1.50105	1.49-1.51	5.9
Di-aromatics	1.51857	1.51-1.53	2.4
Tri-aromatics	> 1.53	> 1.53	1.2

* After Dovgopolyi and Eminov (1968).

It can be assumed that the molecular weight of the products are within the same range of that for the original oil. The nitrogen content determined by elemental analyses of the aromatic concentrates separated chromatographically from the nitrated oil and tri-aromatic blend were 0.2 and 1.75%, respectively. Nitrogen was undetectable in the other two concentrates whose blends underwent attempted nitration.

It is clear that nitration under these conditions proceeds predominantly with the tri-aromatic constituents of the oil. The intermediates of the tri-aromatics formed in this electrophilic substitution reaction possess higher resonance energy (*i.e.* more stable) in comparison to those of the mono- and di-aromatic intermediates. This was furthur confirmed by attempted nitration of pure aromatics under the same conditions of reaction (Al-Sammerai, unpublished results).

Proof of the chemical composition was also gained from the p.m.r. using a Varian-390 (90 mHz) instrument and as shown in Fig. 1. The p.m.r. spectrum of the oil before nitration (a) in carbon tetrachloride shows upfield complex multiplet ($\tau 3 \rightarrow 3.4$) which is attributed to the aromatic protons. High field positioning is due to the shielding effect of the electron releasing alkyl group attached to the aromatic rings. The p.m.r. of the nitrated oil (b) in carbon tetrachloride shows a shift of the multiplet towards down-field ($\tau 2.9 \rightarrow 3.3$). This is due to the electron withdrawing character of the NO_2 groups on the aromatic ring, *i.e.* deshielding effect. The p.m.r. spectrum (c) of the tri-aromatic blend in carbon tetrachloride showed a down-field shift of aromatic protons ($\tau 2.5 \rightarrow 3$) after nitration, this is due to the presence of the NO_2 groups. In comparison, the spectra of mono- and di-aromatics (d) and (e) after attempted nitration showed no change in position of the aromatic protons ($\tau 3 \rightarrow 3.5$) indicating the absence of NO_2 groups.

Evaluation of the products that underwent nitration as corrosion inhibitors was accomplished by assessing the difference in the weight of a standard copper plate before and after 6 hr of immersion in a hot foaming oil at 140°C. The products
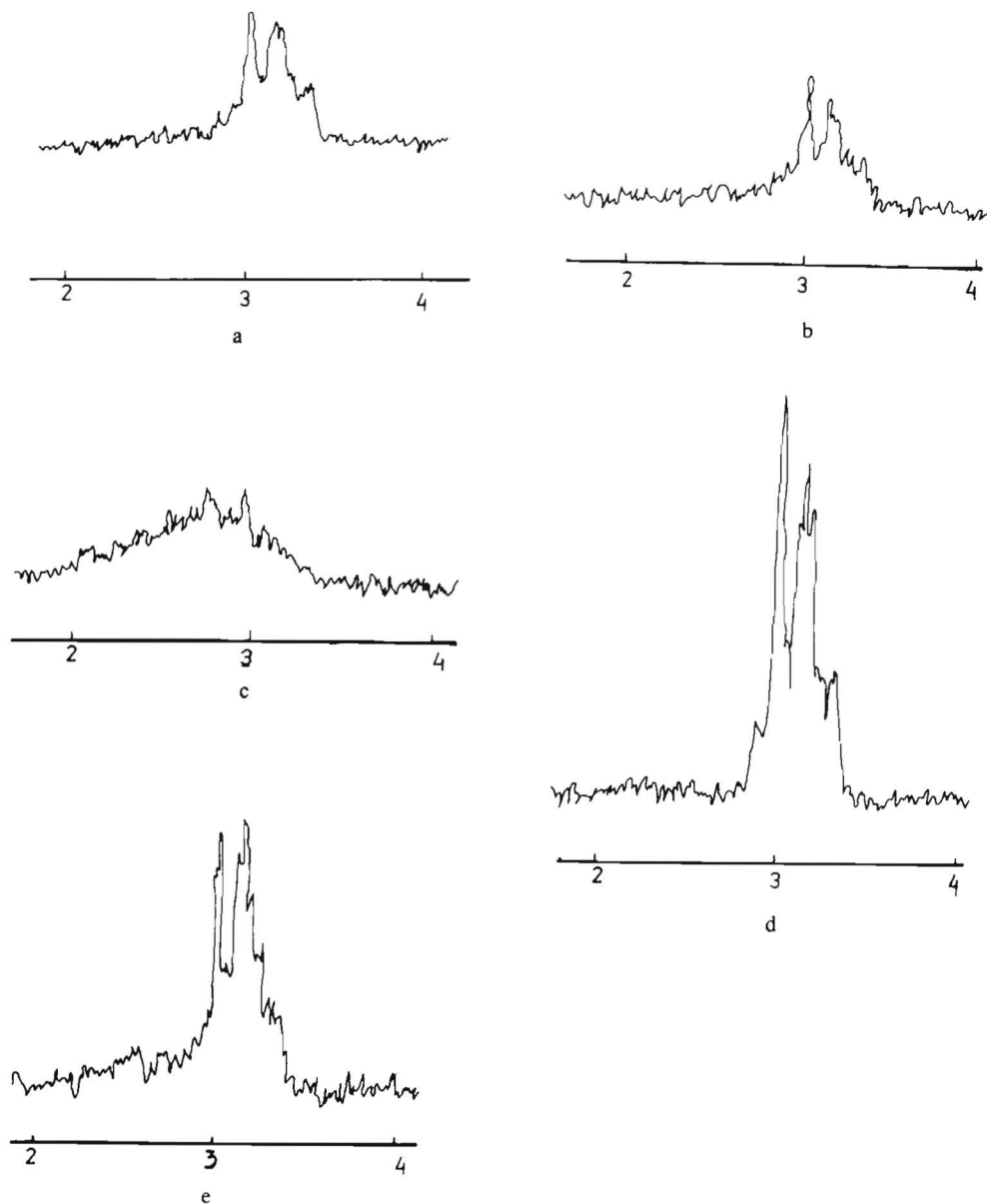
Fig. 1. P.M.R. Spectra in carbon tetrachloride determined on a Varian-390 (90 mHz) instrument:
a. Base oil.
b. Nitrated base oil.
c. Nitrated tri-aromatic fraction dissolved in paraffinic cut.
d. Product from attempted nitration of mono-aromatic fraction dissolved in paraffinic cut.
e. Product from attempted nitration of di-aromatic fraction dissolved in paraffinic cut.

were added in varying concentrations to the test oil, ranging from 2 to 10% by weight.

Figure 2 is a plot of the weight loss of the copper plate expressed in mdd against different concentrations. A sharp decrease in the weight loss of the date is recorded upon addition of about 2% of the nitrated tri-aromatic fraction; the decrease tending to reach zero on increasing concentration. Only a gradual decrease in the weight loss of the plate was recorded upon increasing concentration of the nitrated base oil, and reaching a minimum at about 10% concentration. No marked decrease in the weight loss of the copper plate was observed upon the addition of varying concentrations of the mono- and di-aromatic fractions that underwent attempted nitration.

Since it has been established that the peroxides formed act as oxidising agents in the corrosion of metals (Plate and Boner 1964), nitrated oils can act as corrosion inhibitors indirectly through their effect upon the overall rate of oxidation, *i.e.* peroxide decomposers, or directly through the formation of protective films on the metal surface.
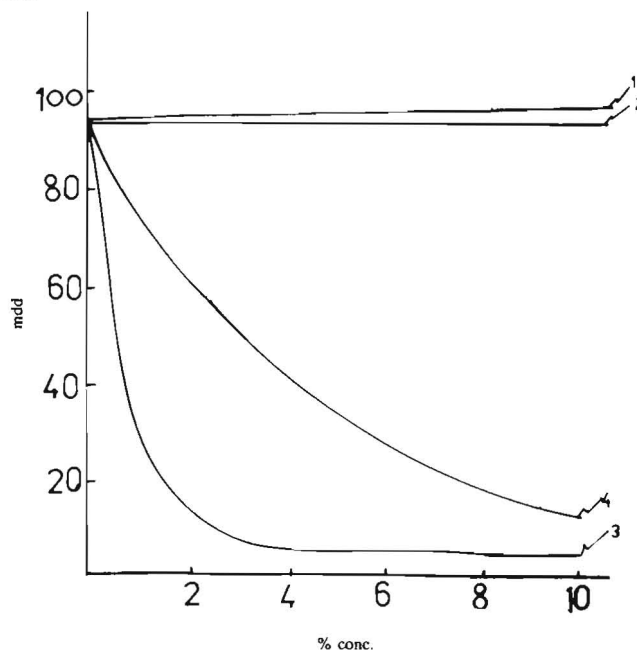

Fig. 2. Difference in weight of loss of copper plate expressed in milligram per square decimeter per day on addition of:
1. Product from attempted nitration of mono-aromatic fraction dissolved in paraffinic cut.
2. Product from attempted nitration of di-aromatic fraction dissolved in paraffinic cut.
3. Nitrated tri-aromatic fraction in paraffinic cut.
4. Nitrated base oil.

Figure 3 is a plot of acidity of the mixture at the end of bubbling time expressed in milligrams potassium hydroxide per one gram of the sample against concentrations of the nitrated products in the test oil. Yet again, only the nitrated oil and to a larger extent the tri-aromatic fraction exhibited a marked decrease in acid number upon their addition.

Conclusion

1. Only the tri-aromatic constituents of the mineral oil are susceptible to nitration under the mild conditions of reaction.

2. The nitrated tri-aromatic fraction exhibited excellent corrosion inhibition in non-aqueous media, even in low concentrations.

3. The choice of feedstock in the manufacture of nitrated oils will be greatly influenced by its aromatic constituents.

References

Al-Sammerrai, D.A. and Ahmed, E. (1980) Nitration of Mineral Oils, *Paper Presented At the Sixth Arabic Conference In Chemistry*, Bagdad, Iraq.
Dolberg, A.L. and Grishaeva, A.S. (1964) Nitration of Mineral Oils, *Khimiya Teknol.*
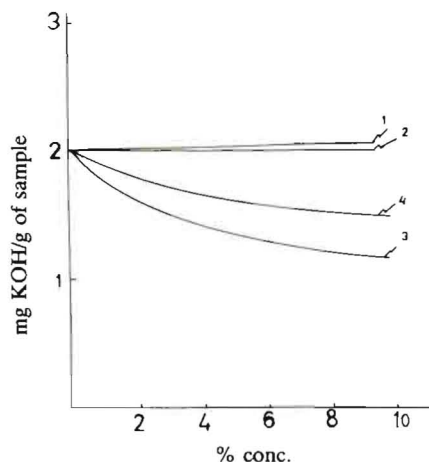

Fig. 3. Changes in acidity of test oil at end of bubbling time expressed in milligram KOH per gram of sample on addition of:
1. Product from attempted nitration of mono-aromatic fraction dissolved in paraffinic cut.
2. Product from attempted nitration of di-aromatic fraction dissolved in paraffinic cut.
3. Nitrated tri-aromatic fraction dissolved in paraffinic cut.
4. Nitrated base oil.

Topl. Masel. **9** (1): 27-32 (*Chem. Abs.* **60**, 14308a, 1964); *ibid.* **9** (9): 33-37 (*Chem. Abs.* **61**, 14440g, 1964).

Dovgopolyi, E.E. and **Eminov, E.A.** (1968) Estimation of the Oxidation Resistance of Inhibited Oils, *Khimiya Teknol. Topl. Masel.* **13** (12): 47-50 (*Chem. Abs.*, **70**, 49191x, 1969).

Finar, I.L. (1973) *Aromatic Nitro-Compounds, Textbook of Organic Chemistry*, Longman, London, 639 p.

Plate and **Boner, C.J.** (1964) *Corrosion Inhibitors in Gear and Transmission Lubricants*, Reinhold Publishing Corporation, New York, p. 82.

Ranney, M.W. and **Al-Sammerrai, D.A.** (1973) *Oxidation and Corrosion Inhibitors, Lubricant Additives*, Noyes Data Corporation, New Jersey, p. 222.

Reshetnikov, S.M. (1970) Use of Nitrated Oils as Anti-Corrosion Additive to Commercial Emulsols, *Khimiya Teknol. Topl. Masel.* **15** (11): 41-43 (*Chem. Abs.* **74**, 55899h, 1971).

Reshetnikov, S.M. (1972) Water-Soluble Products of Mineral Oil Nitration as Inhibitors for Water Corrosion, *Khimiya Teknol. Topl. Masel.* **17** (8): 45-47 (*Chem. Abs.* **78**, 6256v, 1973).

التعرف على مثبطات التآكل النشطة في الزيوت المعدنية المنترتة

نؤيب عبد الجبار السامرائي ، قاسم شوكت مجيد

و وجدان داود محمد سليم

مركز بحوث النفط ـ الجادرية ـ بغداد ـ العراق

ظهـر أن عمليـة نترتـة الـزيـوت النفطية ذات الوزن الجزيئي ٤٠٠ تؤدي إلى تكـوين مثبطـات التـآكل في محيط لا مائي . ولمعـرفـة المادة الفعـالـة في تثبيط التـآكـل تمت محاولة نترتـة الهيـدروكـربـونـات العطـريـة، كل حسب عدد حلقاته، مع حمض النتريك المخفف وبدرجة حرارة ٥٠ مئوية .

تبين أنه تحت هذه الظروف لاتتعرض المركبات العطرية الأحـاديـة والثنـائيـة الحلقة إلى النترتة، بينما تتحول المركبات العطرية الثلاثية الحلقة بسهولة إلى نواتج منترتة .

إن خاصيـة منـع التـآكـل للزيوت المنترتة تُعزى بدرجة رئيسية إلى وجود هذه المركبات .