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Deformulation of metalworking lubricants : Organic phosphorus additives characterization by ^{1}H, ^{13}C and ^{31}P NMR

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Abstract. The analysis of two phosphate ester additives found in the formulation of metalworking fluids is reported. These are isopropylated triarylphosphates which are used as extreme pressure additives and polyethoxylated phosphates with emulgating properties. The additives are first analyzed as raw materials; then within a typical lubricant where they are identified and quantified. The methodology makes use of chromatography (TLC, HPLC, SPE) and NMR spectroscopy (^{1}H, ^{13}C, ^{31}P). The valuable contribution of ^{31}P NMR to the deformulation of such products is particularly emphasized.

Key words. Metalworking fluid – Deformulation – ^{31}P NMR – Phosphate ester – Extreme pressure additive

Introduction

Lubrication influences the effectiveness and the overall efficiency of various metal forming and metal cutting processes such as rolling, extrusion, drawing, forging, sheet-metal forming, broaching, gear shaping, milling… [1]. It should primarily reduce friction, which generally affects tool life, metal flow, energy consumption, heat evolution and surface finish. Modern lubricants are formulated from a range of base fluids (70 % to 80 %) and chemical additives (20 % to 30 %) [2]. The base fluids involve most commonly mineral oils (paraffinic, naphtenic, aromatic oils) or synthetic oils. Additives are chosen for their ability to perform one or more specific functions [3], [4]: anti-wear, extreme pressure agents, corrosion inhibitors, load-carrying additives, wetting agents, emulsifiers, biocides… Except for severe cutting or forming operations, the oil concentrate (base oil + additives) is generally diluted with water. Such oil-in-water emulsions containing 2 % to 5 % of concentrate, reduce the lubricant cost, improve its cooling efficiency and limit smoke and fire hazards.

It is a matter of prime importance for the manufacturers or the consumers of lubricants to control or analyze their composition and their properties. Such a job is required as *quality control checks* to ensure uniformity of product quality to meet a series of performance specifications. A best knowledge of rival chemicals is also gained as part of the competition among additive producers. Finally the lubricant can also be followed at different periods of its life: storage, use, ageing, recycling…

The isolation, the identification and the titration of all or part of the components of the base oils constitute a tremendous analytical challenge due to their number (between 10 and 30) and their great chemical diversity (hydrophobic oils, emulsifiers, mineral derivatives, organic and macromolecular additives). This complexity is still increased as the raw materials can often be made of a mixture of isomers, homologs and parent molecules. To take up such a challenge one has not only to make use of adapted separative and spectroscopic techniques but also to have a thorough knowledge of the lubricants formulation. It is why the term of *deformulation* matches better this kind of work than analysis.

The first step in the deformulation of such complex blends is to check off and to characterize the raw materials, which enter its composition. A particular care will be devoted to the additives which have considerably improved the properties of lubricants and their performance in service during these last ten years: the wetting agents [5], the extreme pressure additives [6] and the macromolecular compounds [7].

We have characterized by means of chromatography techniques (TLC, HPLC, ion-exchange SPE) and

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NMR spectroscopy (^1H, ^{13}C and ^{31}P) two typical organo-phosphorus additives. The first one is a triarylphosphate used as an extreme pressure agent, and the second one is a polyethoxylated phosphate ester with emulgating properties. Their behaviour within a standard lubricant is then studied.

Results and discussion

Extreme pressure additives (EP)

The extreme pressure additives most commonly used include organo-phosphorus esters, sulfur-containing derivatives and chlorinated hydrocarbons. They lead, at high temperatures, to the formation of a film at the tool-workpiece interface during the metalworking process. This film minimises friction whilst controlling wear.

Among the phosphorus additives, the physical and chemical properties of the phosphate esters – $O = P(OR)_3$ – can be varied considerably depending on the nature of the R-substituents (alkyls and/or aryls). Furthermore, they are easily flushed away at the end of the machining operation by water rinsing according to their emulsifying ability.

Isopropylated triphenylphosphate

The product under study is named Reofos™ (R) 65 (Fig. 1) and is marketed by FMC Corporation (Philadelphia, PA, USA). According to its material safety data sheet it contains 10 % to 30 % of triphenylphosphate (TPP) and 60 % to 100 % of isopropylated triphenylphosphate. No information was available concerning its synthesis. The UV-visible spectrum shows two absorption maxima: λ_{max} = 210 nm and 269 nm.

Generally, such compounds are prepared from phenols by propylation of the latter followed by phosphatation. The method leads to a mixture. Its composition depends upon experimental conditions (type of reactants, of catalytic material, of phosphating reagent…). [8], [9], [10].

The "natural" esters are generally prepared from complex mixtures of cresols and xylenols derived by distillation of coal tar fractions. The vast majority of modern phosphate esters are "synthetic" using materials derived from petrochemical sources. Isopropylated or t-butylated phenols are produced from phenols by reaction with propylene or butylene. The most frequently employed phosphating agent to yield the crude product is $POCl_3$, but it can be replaced by H_3PO_4 or PCl_5.

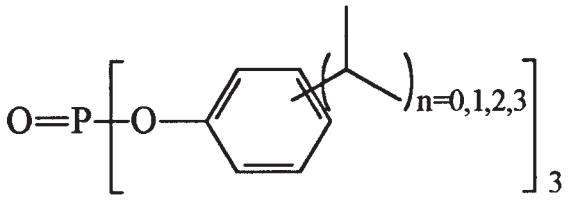

Fig 1. Generic formula of Reofos™.

Direct analysis

The ^1H NMR spectrum of Reofos™ (Fig. 2) confirms that the aromatic ring bears isopropylated substituents. Two distinct groups of aliphatic protons appear at δ = 1.12 and 1.22 ppm (doublets - C$\underline{H}_3$) and at δ = 2.89 and 3.18 ppm (heptuplets - C$\underline{H}$). By analogy with the spectra of the different isomers (o-, m-, p-) of isopropylphenol, we conclude that our Reofos™ sample contains orthosubstituted derivatives of TPP (1.12 and 3.18 ppm) and para- and/or meta-substituted derivatives which have very close chemical shifts and cannot be distinguished (1.22 and 2.89 ppm). By integration of these signals it can be established that, among the substituted TPP, 45% (mol/mol) are ortho derivatives and 55% are para and/or meta derivatives.

Furthermore, the aliphatic protons-aromatic protons (pattern - 6.90 to 7.50 ppm) integrals ratio indicate that the average number of isopropyl groups by molecule is 1.6.

The ^{13}C NMR spectrum also distinguishes the ortho ($\delta\underline{C}H_3$ = 22.8 ppm and $\delta\underline{C}H$ = 26.7 ppm) and the para- and/or meta positions ($\delta\underline{C}H_3$ = 23.8-24.0 ppm and $\delta\underline{C}H$ = 33.5-33.9 ppm) of the isopropyl substituents. The TPP (Fig. 1, n = 0) is identified by its four peaks (δ = 120.1; 125.6; 129.8 and 150.5 ppm) by comparison with an authentic sample of this derivative.

By ^{31}P NMR (Fig. 3: the ^1H coupled and decoupled spectra are similar) about fifteen signals (five strong signals, four medium, the others being weak) are observed in the range $\delta \approx$ -16.0 ppm to $\delta \approx$ -17.0 ppm. Such chemical shifts are in accordance with the presence of at least 15 different triarylphosphates, among which TPP (δ = -17.0 ppm) represents 18 % (mol/mol) of the total composition of Reofos™ .

The reverse-phase HPLC analysis of Reofos™ (Fig. 4) confirms the presence of at least twenty different molecules, which can be divided into four distinct patterns (G_i, i = 1-4) and a single peak G_0 (r_t = 81 min). For all these peaks, higher UV-absorbance at 269 nm than at 240 nm confirms the presence of a phenyl group in each detected molecule.

The different G_i patterns ($i \neq 0$) with higher retention times (r_t) than TPP suggest that they correspond to more hydrophobic molecules bearing substituents on their aromatic rings. As an example, when excluding the trisubstituted derivatives, 14 mono- and disubstituted derivatives are expected according to the generic formula given in figure 1.

Analysis after separation

Reofos™ was analyzed by TLC in order to get more information about its chemical composition. Four fractions F_i (i = 0-4), indexed by increasing R_f-values, were collected after extraction from silica by methanol and analyzed by HPLC, ^1H and ^{31}P NMR (table I). Similar results are obtained through flash chromatography separation.

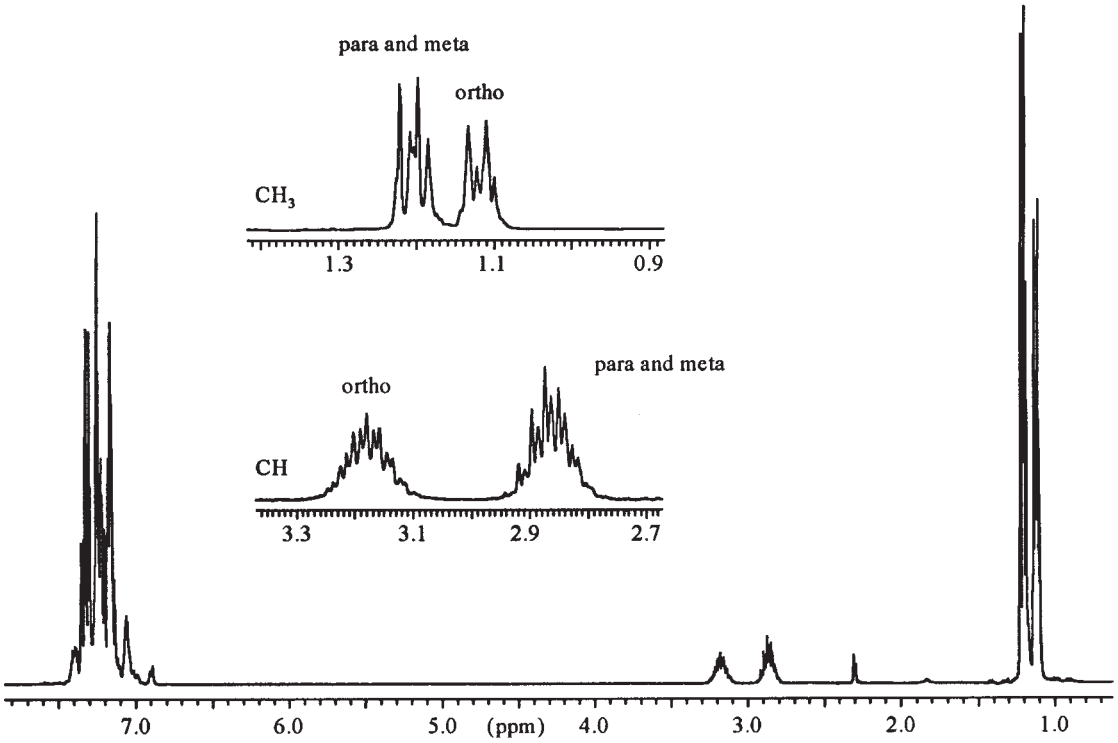

Fig 2. ^{1}H NMR spectrum of Reofos™ in $CDCl_3$.

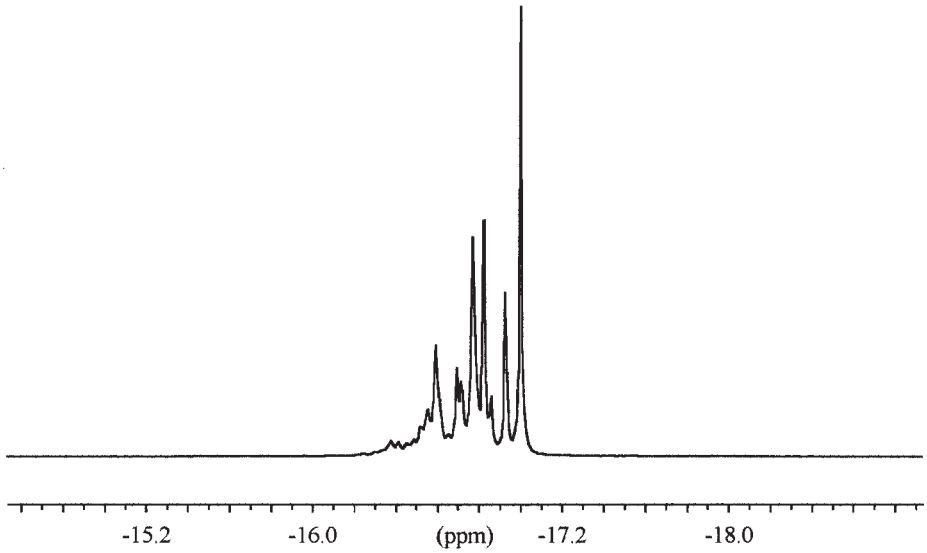

Fig 3. ^{31}P NMR spectrum of Reofos™ in $CDCl_3$.

The integration of the ^{1}H NMR signals gives the ratio r between the numbers of isopropyl groups and aromatic rings. So, it can be concluded that the fraction F_3, showing an HPLC chromatogram similar to pattern G_4 (see Fig. 4), mainly contains trisubstituted TPP (r = 1.2; 15 % -w/w- of Reofos™). The lower ratios for F_2 (r = 0.83) and F_1 (r = 0.42) are in accordance with lower R_f-value for these fractions as the number of isopropyl groups is decreasing. The complexity of the corresponding HPLC chromatograms (covering the G_1 to G_4 patterns) is related to the position of this group on the aromatic ring (o-, m- or p-) [11], [12].

This complexity is still present in the ^{31}P NMR spectra due to the very high sensitivity of the chemical shift both to the rate and the position of the substitution on the aromatic ring by the isopropyl group as it is reported for the o-, m-

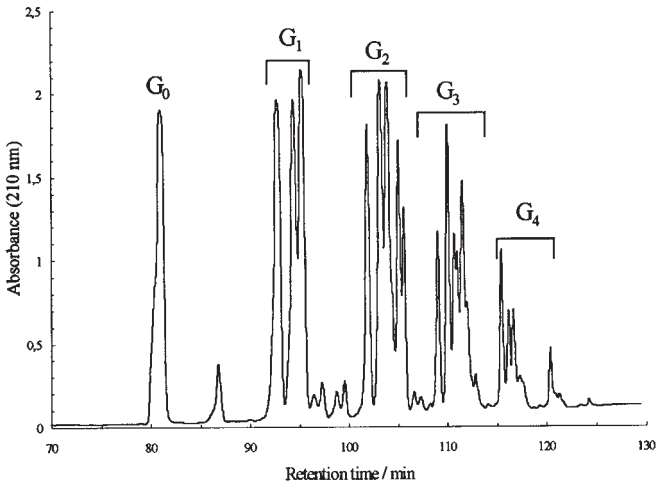

Fig 4. HPLC chromatogram of Reofos™.

and p-tritolylphosphate [13] where each isomer gives a different signal. It can be mentioned that the signals are deshielded when the number of isopropyl groups increases as the signal of TPP is resonating at the highest field.

Finally, it should be noticed that, beside TPP – δ (^{31}P) = -16.98 ppm – and two other phosphorus derivatives – δ (^{31}P) = -16.95 and -16.71 ppm – very likely to be mono-substituted TPP (o- and p-/m-isopropylTPP – r = 0.33 – table I), the fraction F_0 (patterns G_0 and G_1) also includes no P-containing products. The ^{1}H NMR spectrum of the latter consists of two very close singlets around 2.3 ppm (see Fig. 1) and another one at 7.1 ppm. These signals represent only 2 % (mol/mol) of Reofos™ and indicate the presence of residual methylated phenol derivatives (cresols and/or xylenols) which were probably used for the synthesis of Reofos™.

So, we can conclude that the analyzed Reofos™ sample is a complex mixture of TPP (18 % – molar ratio) and isopropylated triarylphosphates (82 %). The average rate of substitution is 1.6 and about fifteen molecules can be counted. The isopropyl substituting group is in the ortho position for 45 % of the substituted molecules, and in the para and/or meta position for 55 % among them.

The knowledge of the rate of substitution is particularly a key information for the use of such additives. The weight ratio between the aryl groups bearing an alkylated substituent and the non-substituted aryl groups must be controlled as it influences the homogeneity and the viscosity of the additive [8], [9]. These last parameters should be adapted to each specific use: plasticiser, formulation of hydraulic fluids, combustibles or, as in our case, of lubricants where it would be favourable to increase this rate.

Emulsifiers

This class of additives includes derivatives with a polyethoxylated chain as hydrophilic group and a long hydrocarbonated chain (such as arylnonyl) as lipophilic group. Their role is to stabilize the emulsion, to ensure better lubricity and to clean sheet metal surfaces by removing metal chips.

Ethoxylated arylphosphate

The studied product is marketed under the name Lubrhophos™ LM-400 by Rhône-Poulenc (Cranburry, NJ, USA). According to its material safety data sheet it is a poly(oxy-1,2-ethanediyl)α-(dinonylphenyl)ω-hydroxyphosphate (Fig. 5). The presence of free OH groups is detected by IR spectroscopy. The UV-visible spectrum shows three absorption maxima: λ_{max} = 207 nm, 226 nm and 277 nm.

Direct analysis

Three distinct patterns are observed on the ^{1}H NMR spectrum of Lubrhophos™ (Fig. 6).

The first one, between 0.6 and 1.8 ppm, corresponds to the aliphatic protons of the nonyl group (H_{aliph}). The second one characterizes the CH_2 groups of the polyethoxylated chain (H_{meth}). One can distiguish (i) those which are close to the phosphorus atom P-O-C$\underline{H}_2$ (δ = 4.2 ppm) and P-O-CH_2-C$\underline{H}_2$ (δ = 4.1 ppm) (ii) those which are close to the aromatic ring C$\underline{H}_2$-O-Ar (δ = 3.9 ppm) and (iii) those of the polyethoxy link -(C$\underline{H}_2$-C$\underline{H}_2$-O)$_n$- (δ = 3.7 ppm). The third

Table I. HPLC and ^{1}H and ^{31}P NMR data of the F_0, F_1, F_2 and F_3 fractions isolated by SPE.

	HPLC	*^{1}H NMR*	*^{31}P NMR - δ / ppm*			
Fraction (w/w)	Pattern	$r = \frac{\text{aliphatic groups}}{\text{aromatic rings}}$	-16.48	-16.71	-16.95	-16.98
F_0 (5 %)	G_0, G_1	0.33		+	+	+
F_1 (40 %)	G_1, G_2, G_3	0.42		+	+	+
F_2 (22 %)	G_3, G_4	0.83	+	+	+	
F_3 (15 %)	G_4	1.20	+	+	+	

A + indicates the presence of the signal with the corresponding chemical shift.

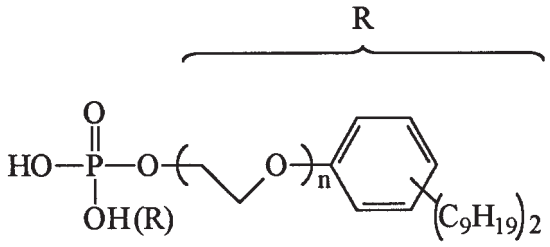

Fig 5. Generic formula of Lubrhophos™.

pattern represents the aromatic protons (6.7 ppm < δ < 7.2 ppm; H_{arom}) and a singlet (δ = 7.3 ppm; H_{hydr}). This last singlet disappears when a drop of D_2O is added in the NMR tube and its chemical shift is very sensitive to the pH-value. This is in agreement with the presence of free OH functions.

The lack of signals in the 2.5-3.0 ppm region points out that the nonyl group is neither bound to the aromatic ring through a methylene group (R-C$\underline{H}_2$- Ar, δ ≈ 2.6 ppm) nor a methine group (R(R')CH- Ar, δ ≈ 2.8 ppm). This is indicative of a certain degree of branching of the alkyl chain.

On the other hand the ratio between the integrals of the aliphatic and aromatic protons patterns (H_{aliph}/H_{arom} ≈ 12.0) points out that there are, on average, two nonyl groups on each aromatic ring (for a dinonylphenyl, the theoretical value of the ratio should be 38/3 = 12.7). The ratio H_{aliph}/H_{meth} ≈ 1.2 corresponds to eight ethoxylated links (the theoretical value should be 38/32 = 1.2). Lastly, the ratio H_{arom}/H_{hydr} ≈ 1.3 shows that there are two OH groups for one phosphorus atom (theoretical value = 3/2 = 1.5). Hence the phosphate monoester should be the prevalent ester in Lubrhophos™.

The ^{31}P NMR spectrum (Fig. 7) consists of three rather broad signals (δ = 0.54 ppm; 1.45 ppm and 2.09 ppm) so that the phosphorus atom is at least in three distinct electronic surroundings. The peak at 2,09 ppm is nevertheless very small (< 5% - mol/mol).

If triethylamine (TEA) is progressively added, these signals become narrower and undergo a downfield shift. The deshielding is more important for the main peak at 1.45 ppm than for the second peak at 0.54 pmm. With an excess of TEA, these peaks are respectively at 2.56 and 0.90 ppm. This is typically observed with phosphate esters. Their chemical shifts vary in the range +5.0 and -3.0 ppm and a broadening and an upfield shift is observed when the pH-value of their solutions is lowered [14]. Thus, the sample of Lubrhophos™ is a mixture of 60 %-65 % (mol/mol) of monoesters (δ = 1.45 ppm, in the range +4.8/-2.2 ppm) and of 30 %-35 % of diesters (δ = 0.54 ppm, in the range 1.1/-3.0 ppm). When an excess of TEA is added, the dianion of the monoester (δ = 2.56 ppm) and the monoanion of the diester (δ = 0.90 ppm) are formed. Their chemical shifts are respectively in the range 2-5 ppm and 0-1 ppm as reported in literature data [14]. 5 % of residual phosphoric acid (δ = 2.09 ppm) is also present in Lubrhophos™.

The HPLC analysis of Lubrhophos™ at 210 nm shows two not well-resolved peaks with retention times of 120 and 122 min respectively. The similar outlines of these peaks

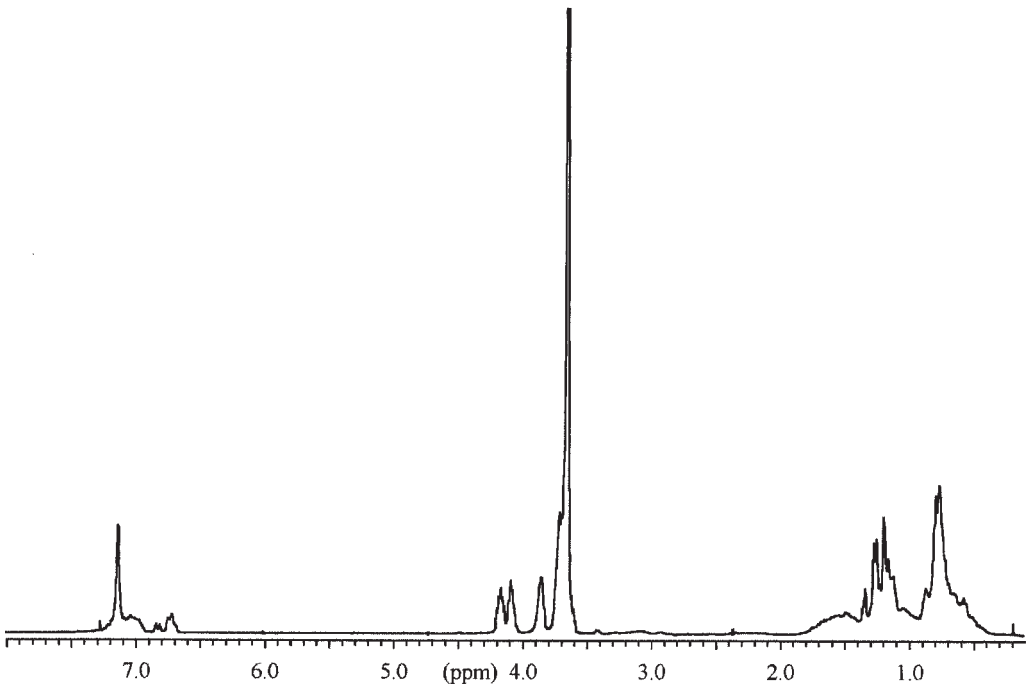

Fig 6. ^1H NMR spectrum of Lubrhophos™.

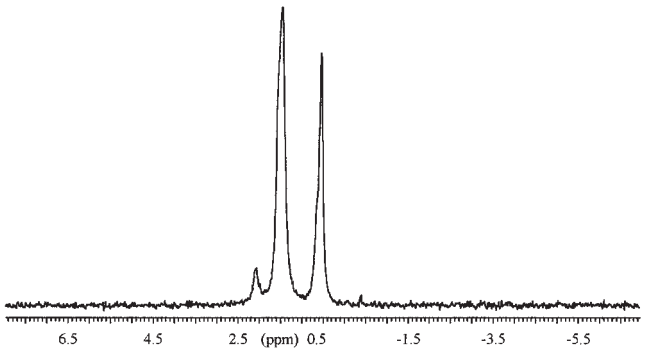

Fig 7. ^{31}P NMR spectrum of Lubrhophos™.

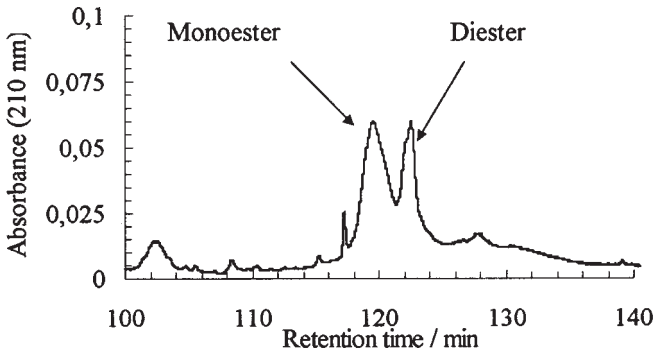

Fig 8. HPLC chromatogram of Lubrhophos™.

when detected at different wavelengths and the presence of a secondary maximum at 280 nm is indicative of two closely related chemical species, possessing each aromatic moieties.

The mass spectrum confirms that Lubrhophos™ contains a mixture of mono- and diesters, but no triesters. Furthermore the length of the polyethoxylated chain of each ester has a gaussian distribution from n = 2 to n = 15, but it is mainly found between 6 and 10.

Analysis after separation

The separation of the mono- and diesters was achieved by means of ion-exchange chromatography. An excess of triethylamine (TEA) is added to Lubrhophos™ to neutralize its acidic functions. The solution is then eluted through a silica anion-exchange column first with methanol, then with diluted hydrochloric acid. Two fractions are collected.

The ^{1}H and ^{31}P NMR spectra of each fraction show that they contain separately one of the two phosphorus derivatives present in Lubrhophos™.

The first fraction should contain the diesters which, despite the neutralization of their acidic function, are not retained on the column. They are characterized by the ^{31}P NMR signal resonating at higher field and the HPLC peak having a retention time of 122 min as confirmed by an analysis of this fraction by each technique. On the other hand, the monoesters are found in the second fraction as they are fixed on the column by their two negative charges, being then eluted with the hydrochloric acid solution. The less shielded ^{31}P NMR signal and the HPLC peak with the retention time of 120 min characterize this fraction.

So, we can conclude that the analyzed Lubrhophos™ sample is a mixture of 60 % to 65 % (mol/mol) of monoarylpolyethoxyphosphate and of 30 % to 35 % of diarylpolyethoxyphosphate. Less than 5 % of residual phosphoric acid was found. The aryl sustituent is a dinonylphenyl group with a branched aliphatic chain and the polyethoxylated chain is made of an average of eight links.

The molecular ratio between the mono-and the diesters as well as the polymerization rate of the ethoxy link are very critical parameters regarding the emulsifying properties [13], [14]. The lubricating efficiency and the emulsion stability (see below) are directly related to these parameters which should be carefully controlled.

Standard lubricant

We have applied this methodology to a standard lubricant, which is in its industrial development stage. It contains the two studied phosphorus additives. It appears that a demixtion of the lubricant occurred during storage. As mentioned above, this problem should be related to the nature of the emulsifier.

^{31}P NMR spectroscopy allows a direct analysis of the crude lubricant by revealing only those molecules bearing at least one phosphorus atom, the number of which being generally limited. By comparison of the spectra with those of authentic samples, the identification and the titration of a given additive is then easily achieved.

The ^{31}P NMR spectrum of the standard lubricant is given in figure 9. The presence of Reofos™ is clearly detected (peaks around -17.5 ppm - see fig.3). No signal referring to Lubrhophos™ is observed, but supplementary signals around 96 ppm and -11 ppm are revealed (the peak at 0 ppm corresponds to 85 % H_3PO_4 used as external chemical shift reference).

As demixtion occurred after a storage period, we have reformulated the oil concentrate of the original lubricant according to its given composition. We followed then its behaviour in ageing (Fig. 10).

The ^{31}P NMR spectrum recorded just after the mixing of each constituent (Fig. 10a) clearly shows the presence of both Reofos™ and Lubrhophos™. Ten days later, a slight hump is observed around -11 ppm. It becomes a more complex pattern after one month as, correlatively, the signals due to Lubrhophos™ have decreased (Fig. 10b). This pattern is

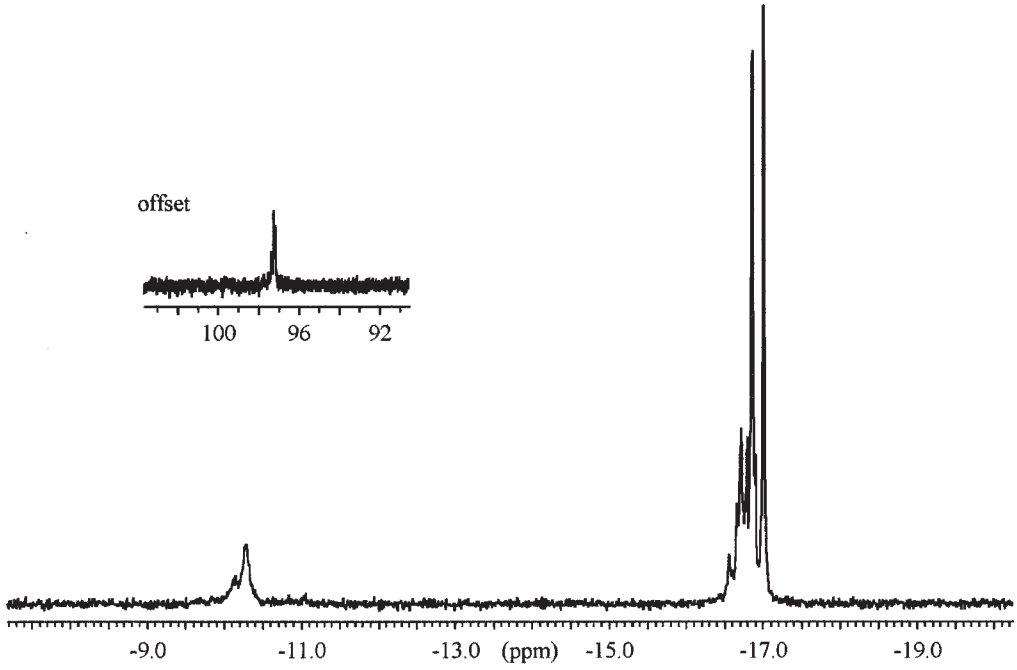

Fig 9. ^{31}P NMR spectrum of the standard lubricant.

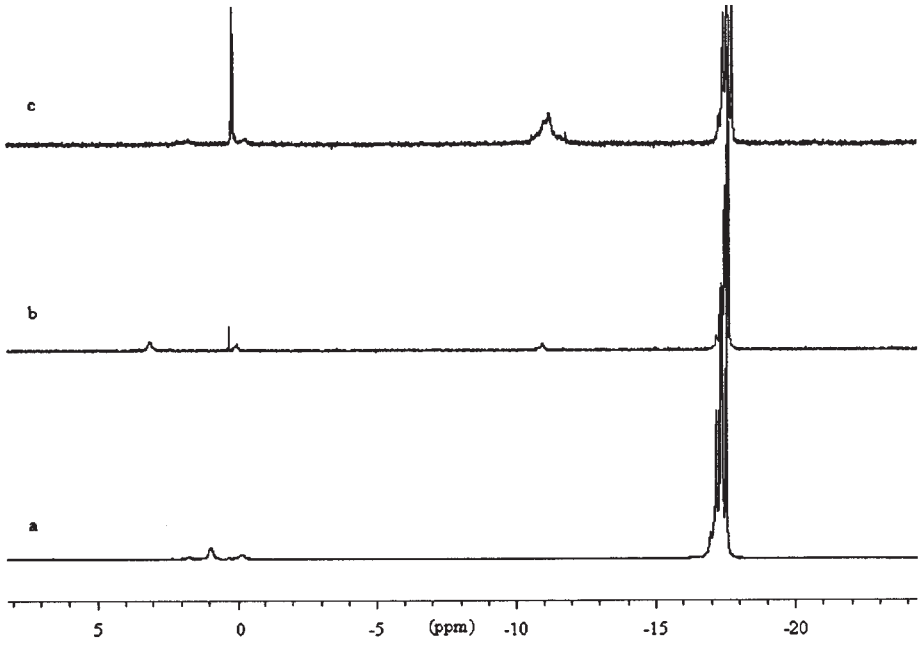

Fig 10. Stability of the standard lubricant as a function of time (RMN ^{31}P). a: t = 0; b: t = one month (ambient temperature); c: t = ten days (80 °C).

similar to the one appearing in the spectrum of the standard lubricant (Fig. 9).

If the reconstituted lubricant is stored one week in a drying oven at 80 °C, the signals of Lubrhophos™ have completely disappeared and have been replaced by the pattern around -11 ppm (Fig. 10c). This last one can be assigned to

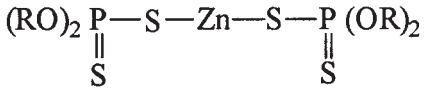

Fig 11. Formula of zinc dialkyldithiophosphates.

polyphosphates (-P-O-P-) resulting from a slow phosphate condensation [8].

The ^{31}P NMR spectra of each of the two phases resulting of the demixtion of the emulsified standard lubricant have shown that the molar ratio between the emulsifier (Lubrhophos™) and the extreme pressure additive (Reofos™) was 20/80 in the upper prevailing phase (pale yellow) and 80/20 in the lower phase (brown). This result outlines that the lower phase is containing in part the polar additives such as Lubrhophos™ (or its evolution products) and that the instability of Lubrhophos™ probably causes the spontaneous demixtion of the lubricant.

The second pattern around 97 ppm (Fig. 4c) lies in the chemical shift range of the compounds possessing P-S bonds. It is tentatively assigned, in comparison with literature data [15], to derivatives which should be closely related to zinc dialkyldithiophosphates (Fig. 11). These latter have antiwear and rather good anti-oxydative properties and are also widely used in lubricant formulations. Their presence seems to be quite fortuitous here.

So, ^{31}P NMR spectroscopy is a valuable tool for the analysis of a given organophosphorus compound and its detection in the blends of lubricant [16]. It can also be used to follow its stability during the lifetime of the lubricant throughout its storage period or its use in machining. A survey of the structural modifications resulting from interactions with other additives (e.g. acid-base reactions, see above) and of products resulting from its degradation [17] can, for example, contribute to bring improvements in additive performances.

Conclusion

The ^{1}H and ^{31}P NMR spectroscopy offers a quick and accurate method for the identification and quantitation of phosphorus-containing additives in metalworking lubricants. A detailed analysis of each additive (which are often themselves complex mixtures) can be performed to get information about parameters (substitution or polymerization rates…) which will directly influence the efficiency of the additive. The study can be done at ambient temperature, without prior separation which can be tedious and time-consuming. The full identification of each homolog in a given additive cannot be achieved, but this is generally not necessary. This methodology could be easily extended to the deformulation of other types of lubricants, since various organophosphorus derivatives (phosphates, phosphites, phosphamines, thiophosphates…) are incorporated as performance additives. The scale of the ^{31}P chemical shifts is very broad (from -300 to +200 ppm) and the phosphorus nucleus is very sensitive to small variations of its electronic environment. So, very subtle differences in molecular structures can be generally displayed without signal overlap. Interactions with other additives can also be studied and impurities or degradation products related to the ageing or the use of the lubricant can be detected.

Materials and methods

Solid phase extraction (SPE)

SPE-SAX (Supelco Inc., Bellefonte, PA, USA) columns are used. 54 mg of Lubrhophos™ and 50 mg of triethylamine are dissolved in 1 mL of methanol. This solution first, 4 mL of methanol secondly and finally 6 mL of 0.1 M hydrochloric acid are successively poured through the SPE-SAX column with a flow of about 1 drop per second.

Flash Chromatography

535 mg of Lubrhophos™ dissolved in 5 mL of hexane are eluted on 10 g of silica (230-400 mesh ASTM, Merck) with 4×20 mL fractions of hexane, hexane-dichloromethane, dichloromethane, ethyl acetate and methanol.

Thin Layer Chromatography

225 mg of Reofos™ are dissolved in 1 mL of methanol and eluted with hexane/dichloromethane (50/50, V/V) on a silica plate (20 cm × 20 cm × 0,2 cm with F_{254} fluorescence indicator, Merck, Darmstadt, Germany). The extraction is performed with methanol.

Reverse-Phase HPLC

A Waters (Milford, MA, USA) HPLC equipped with a 600 E pump, a 490 E multichannel detector and a Millenium® processing system. A C18 Nova-Pack 5 µm column is used. Operating conditions are as follows: solvent flow: 0.7 $mL.min^{-1}$; solvent-gradient from a mixture H_2O / MeOH / H_3PO_4: (80 / 20 / 0.4) to 100 % MeOH in 120 min. The UV-detection is done at 210, 226, 269 and 290 nm. About 200 mg of dry product are dissolved in 1 mL of methanol, then filtered through a 0.2 µm filter before injection.

IR and UV Spectroscopy

IR spectra are run on a Nicolet FT-IR 400-D spectrometer and the UV-visible spectra on a Milton Roy Spectronic 3000 Array spectrophotometer.

Mass Spectrometry

Mass spectra are recorded on a MALDI Finnigan Mat Vision 2000 spectrometer (Laboratoire de Spectrométrie de Masse, UST Lille I, Villeneuve d'Ascq, France).

NMR Spectroscopy

^{1}H, ^{13}C and ^{31}P spectra are recorded on a Bruker AC 300 P FT spectrometer equipped with a QNP probe, operating at 300.13 MHz, 75.47 MHz and 121.50 MHz respectively for each studied nucleus (Laboratoire d'Application RMN, Faculté des Sciences Pharmaceutiques et Biologiques, Lille, France).

The samples are dissolved (0.1 g in 0.5 mL) in $CDCl_3$ (99.8 % D, Eurisotop, Gif-sur-Yvette, France) in 5 mm tubes. ^{13}C spectra are proton-decoupled (CPD-mode). The chemical shifts are reported against TMS (as an internal reference) for ^{1}H and ^{13}C and against H_3PO_4 for ^{31}P (85 % - as an external reference placed in a capillary tube inside the NMR sample tube).

For the ^{31}P quantitative spectra we used triethylphosphonoacetate as the internal standard and 0.15 M $Cr(acac)_3$ as the relaxation agent.

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