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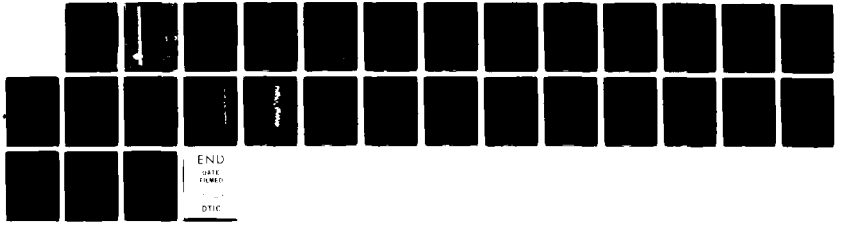

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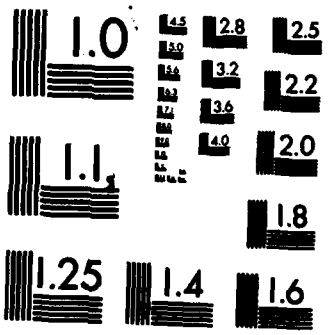

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Report 2372

^{31}P-NMR ANALYSIS OF ZINC DIALKYL(DIARYL)-DITHIOPHOSPHATE IN LUBRICATING OIL

by
Shing-Bong Chen

November 1982

U.S. ARMY MOBILITY EQUIPMENT
RESEARCH AND DEVELOPMENT COMMAND
FORT BELVOIR, VIRGINIA

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

To assure that the oils furnished the government are of the same formulations as the oils originally qualified, a new method has been developed to examine Zinc dialkyl(diaryl)dithiophosphate (ZDDP) additives by using ^{31}P-NMR. Two finished oils and primary alkyl-ZDDP, secondary alkyl-ZDDP, and aryl-ZDDP were examined. ^{31}P-NMR was found to be a better method than other existing analytical methods to analyze the change of ZDDP additives in full formulated oil without pre-separation.

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ILLUSTRATIONS

^{31}P-NMR ANALYSIS OF ZINC DIALKYL(DIARYL)DITHIOPHOSPHATE IN LUBRICATING OIL

I. INTRODUCTION

Zinc dialkyl(diaryl)dithiophosphate (ZDDP) additives are widely used in lubricating oils. The combination of extreme pressure (EP), antiwear, antioxidant, and corrosion-inhibiting properties make ZDDP particularly important in engine lubricants. Both the alkyl and aryl derivatives are employed commercially and are used in Military Specifications MIL-L-2104, MIL-L-46152, MIL-L-21260, and MIL-L-46167 engine oils. The qualified Military Specification oils often use a mixture of alkyl (primary and secondary) and aryl ZDDP in various ratios. The ratio and the amount of different ZDDPs used changed the performance of the engine oils. The aryl derivatives of ZDDP have higher degrees of thermal stability and are used in those environments where higher engine temperature environments are anticipated. Both the antiwear and thermal stability characteristics of the alkyl type ZDDP vary with different alkyl substitutions. The thermal stability of ZDDP followed the order of aryl > primary-alkyl > secondary-alkyl.[1]

To assure that the oils furnished the government are of the same formulations as the oils originally qualified, several analytical methods have been developed. It was reported[2,3] that the ZDDP structure can be determined by the gas chromatograph analysis of corresponding alcohols which are derived from the hydrolysis of ZDDP in nitric acid solution. However, the method may not be satisfactory when the oils contain esters and other organic phosphates which also hydrolyze and give alcohols in acidic solutions. So the indirect analysis of alcohol for ZDDP additive is not conclusive. Differential Infrared (IR) technique was also applied in the report and found that sometimes there is interference by other additives which have absorption peaks in the same region as ZDDP, around 900-1100 cm^{-1}. A liquid chromatography separation of ZDDP from base oil followed by IR analysis was found to be a good method to estimate the amount of aryl-ZDDP but not alkyl-ZDDP in finished oil.[4]

The 100% natural abundance of phosphorus-31 has nuclear spin I = ½ which allows it to be observed in nuclear magnetic resonance (NMR) with high overall sensitivity and with narrow line width as proton-NMR. ^{31}P-NMR has been widely applied in the phosphorus chemistry field for structure determination, qualitative, and quantitative analysis.

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1 R. C. Coy and R. B. Jones, *ASLE Trans.*, *24*, *1*, p. 77 (1979).
2 M. Kolobielski, CCL Report No. 320, AD-757 605, US Army MERADCOM, Ft. Belvoir, VA (1973).
3 G. Jenkins and C. M. Humphreys, *J. Inst. Petrol.*, *51*, p. 1 (1965).
4 G. E. Fodor and F. M. Newman, *ASLE Trans.*, *22*, 4, p. 389 (1979).

The ^{31}P-NMR chemical shifts (δ) of ZDDP are different from most of the other phosphates (triphenyl phosphate, inorganic phosphate, etc.), as large as 100 ppm compared to the resolution of 0.04 ppm in this study. Thus, ZDDPs are readily identified from other types of phosphates and phosphite oil additives.

This report describes a new spectroscopic method to observe the ZDDP additives in finished oil directly without pre-separation. The Differential IR spectra of additives and finished oil were also included.

II. RESULTS AND DISCUSSIONS

1. ^{31}P-NMR and ^{1}H-NMR Studies. The phosphorus Numclear Magnetic Resonance (^{31}P-NMR) and proton-NMR spectra are shown in Figures 1 through 11. The chemical shift (δ) of primary zinc dialkyldithiophosphate (ZDDP, 1P), secondary ZDDP (1S and 2S), and zinc diaryldithiophosphate ZDDP (1A) are as follows:

Chemical Shift (δ,ppm) from Triphenyl Phosphate (TPP), Deuterated Cloroform ($CDCl_3$) Solution:

	δ(ZDDP)	δ(Detectable Impurity)
1P	116.64	120.80
1S	110.70, 110.99	116.36, 116.76
2S	110.75	116.32
1A	112.77	NA

The ^{31}P-NMR spectrum of 1P (Figure 1) showed at least three phosphorus species, the peaks at 120.80 ppm could be the by-product of ZDDP[1]. The ^{1}H-NMR (Figure 2) showed that there were two major primary alkyl ZDDPs which were isobutyl and isopentyl (or n-pentyl) ZDDP and had α-protons' peaks at 3.94 ppm ($J_{H\text{-}P}=8.3$ Hz and $J_{H\text{-}H}=7.3$ Hz) and 4.17 ppm ($J_{H\text{-}P}=8.0$ Hz and $J_{H\text{-}H}=6.7$ Hz), respectively. From the α-proton, the ratio of isobutyl to isopentyl was 3:1. More than a simple pentuplet was found in gated decoupling ^{31}P-NMR spectrum (Figure 3) which supported that more than one ZDDP gave peaks at 116.64 ppm.

The ^{31}P-NMR spectrum of 1S (Figure 4) showed two major peaks at 110 ppm which account for secondary ZDDP. The peak at 116.76 ppm could also be a similar by-product as is the peak at 120.80 ppm of 1P. The peak at 116.36 could be primary ZDDP isomer. The partial peak overlap of primary alkyl-ZDDP and the side product of secondary alkyl-ZDDP (1S) could be further separated by using the paramagnetic lanthanide NMR shift reagents which can shift these peaks in different degrees selectively. The ^{1}H-NMR spectrum (Figure 5) showed peaks at 3.93 and 4.16 ppm which is the expected chemical shift for α-proton of primary alkyl ZDDP. The deduction of ^{1}H-NMR spectrum showed that the two major ZDDPs were isopropyl

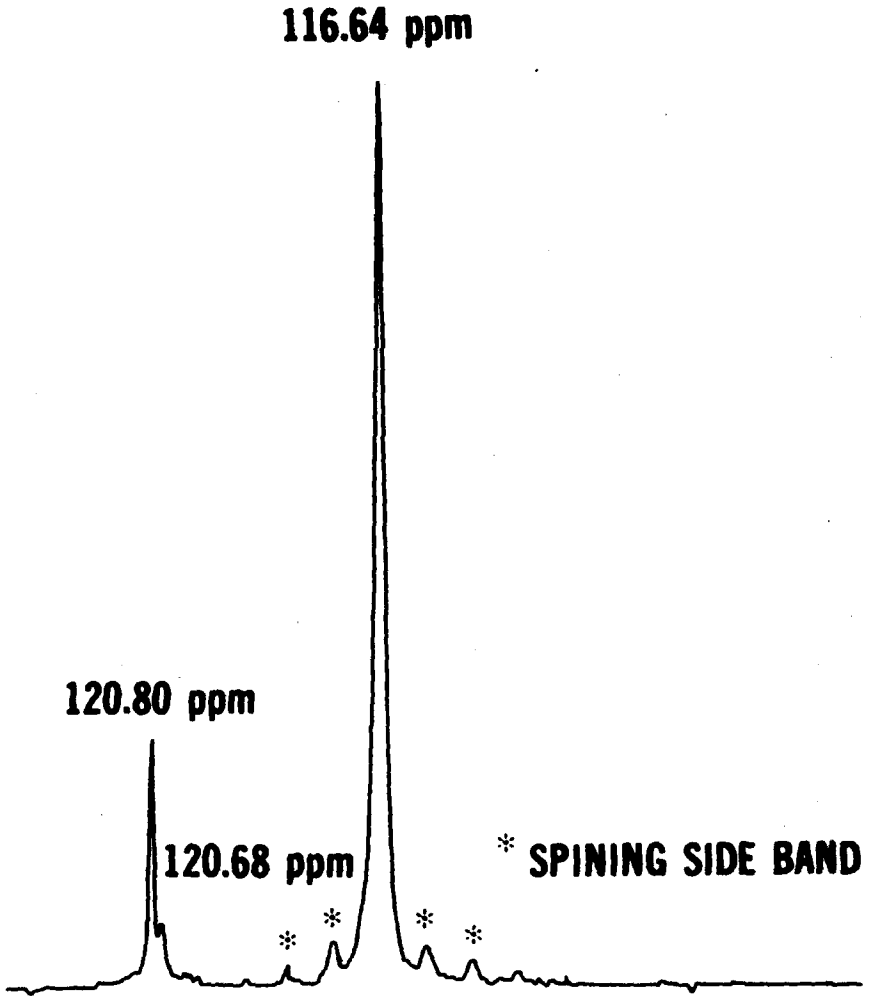

Figure 1. ^{31}P-NMR spectrum of primary alkyl-ZDDP (1P).

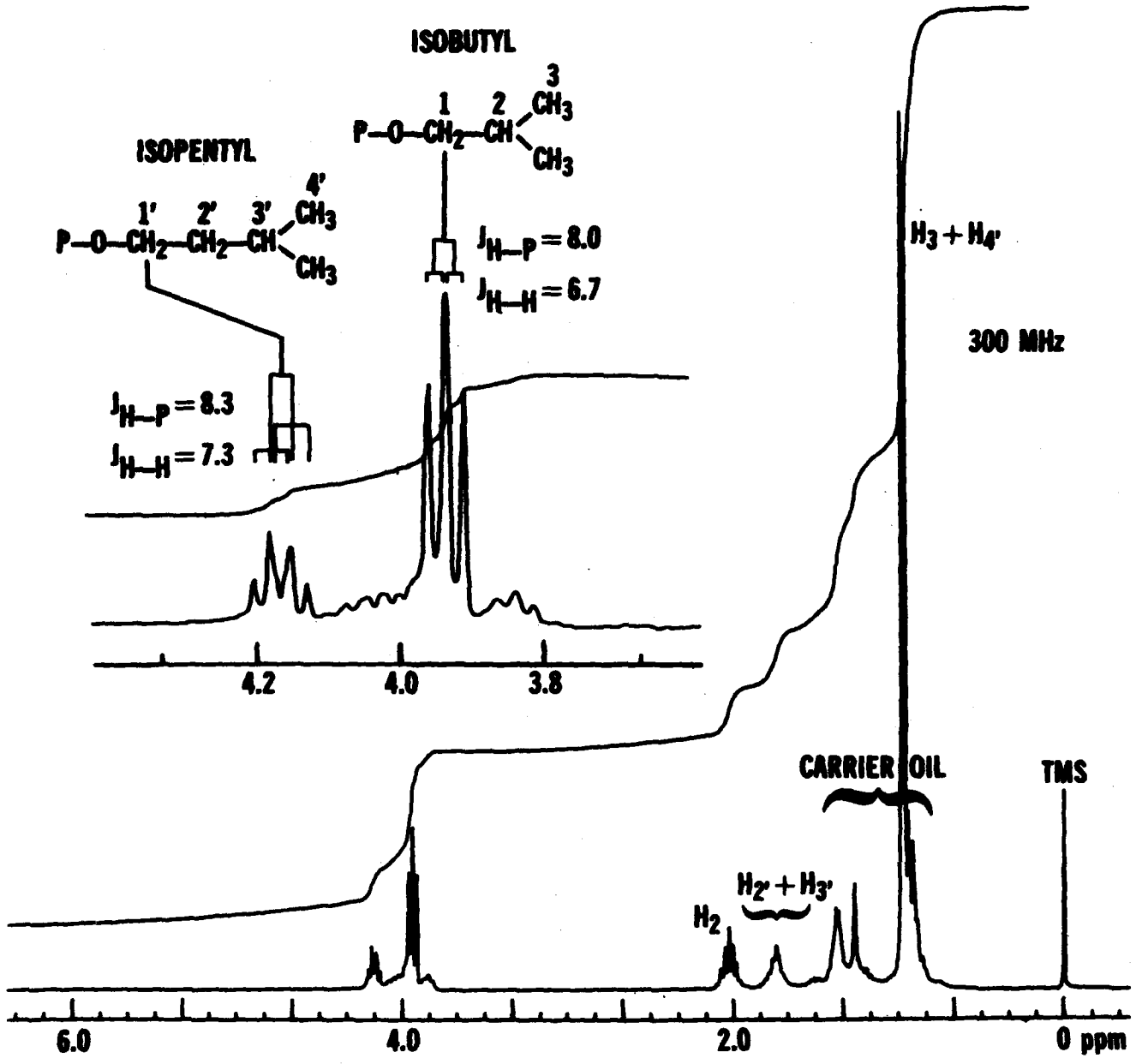

Figure 2. PMR spectrum of primary alkyl-ZDDP (1P).

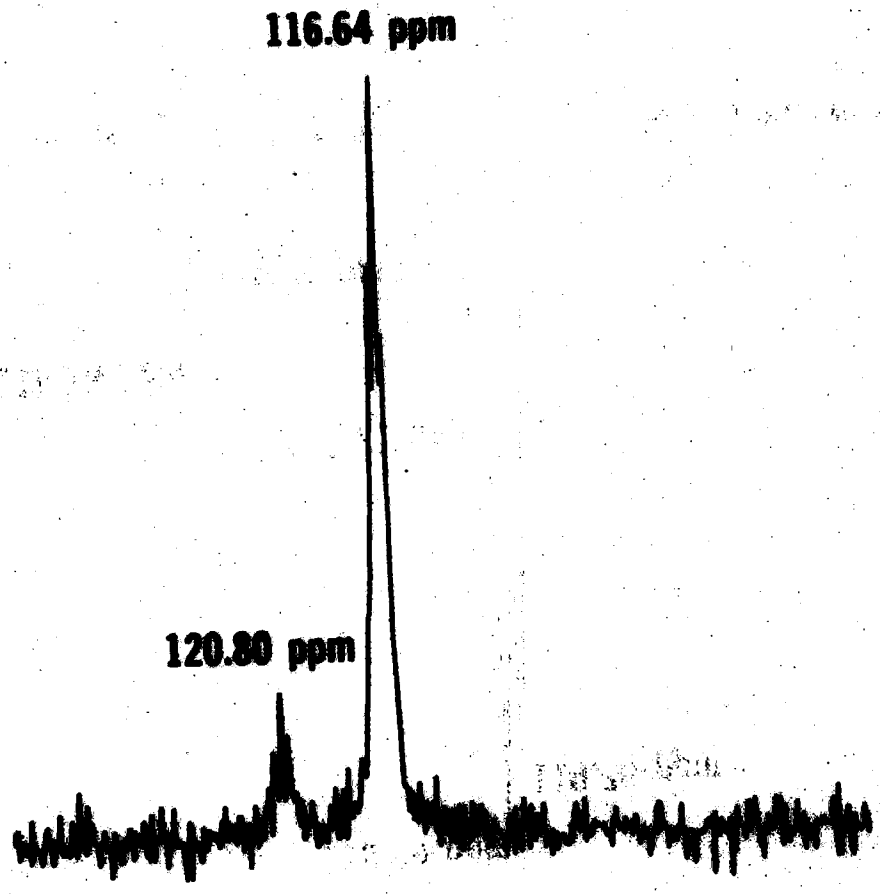

Figure 3. Gated proton decoupling ^{31}P-NMR spectrum of primary alkyl-ZDDP (1P)

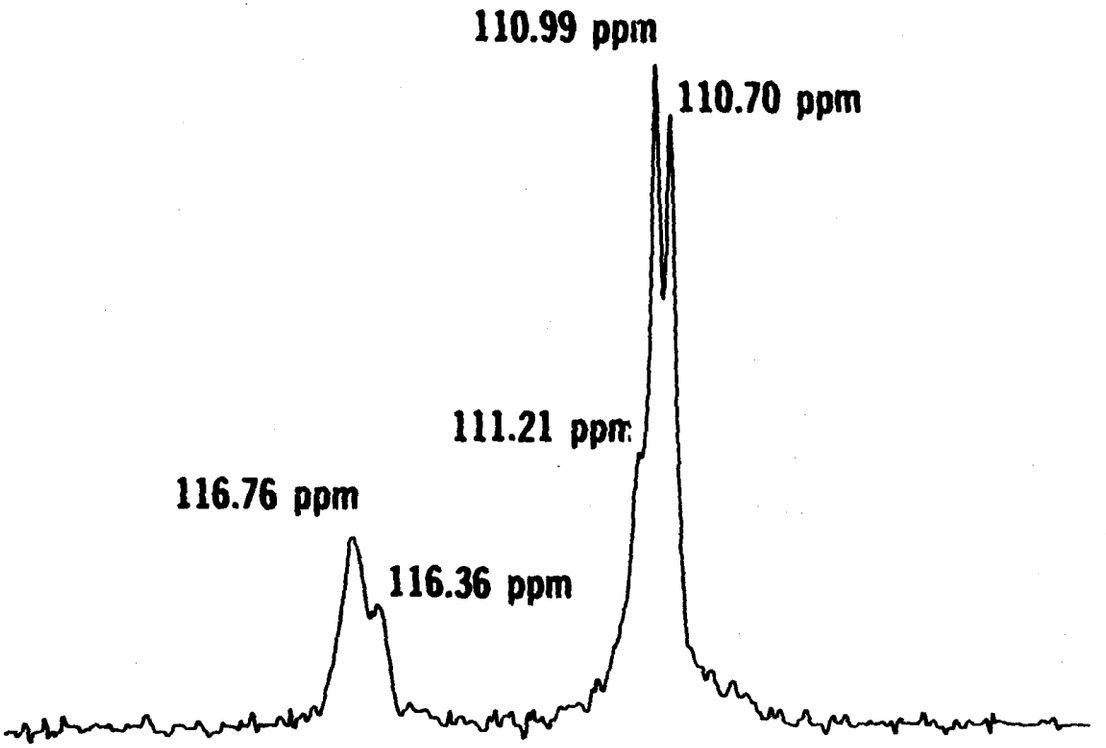

Figure 4. ^{31}P-NMR spectrum of secondary alkyl-ZDDP (1S).

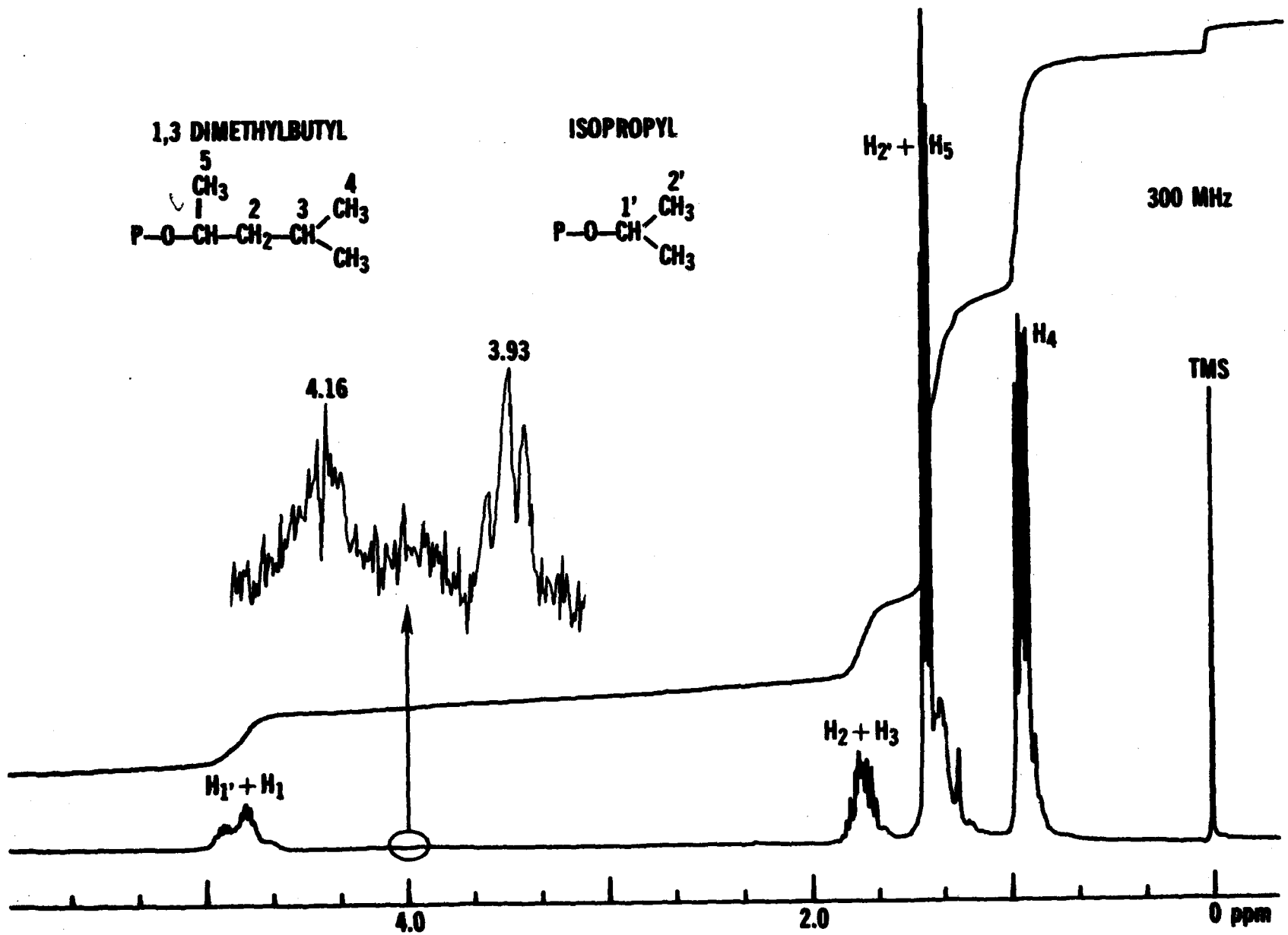

Figure 5. PMR spectrum of secondary alkyl-ZDDP (1S).

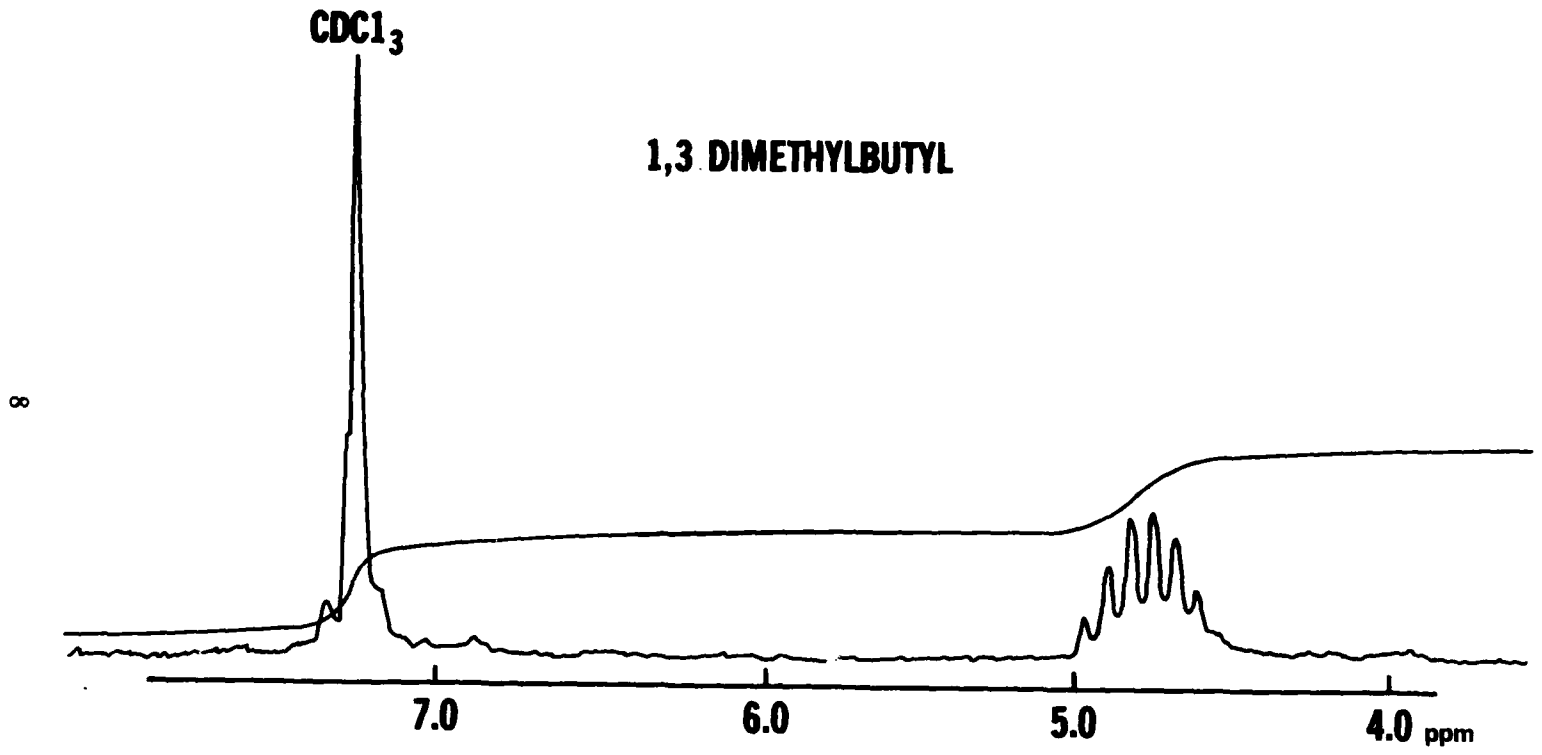

Figure 6. PMR spectrum of secondary alkyl-ZDDP (2S).

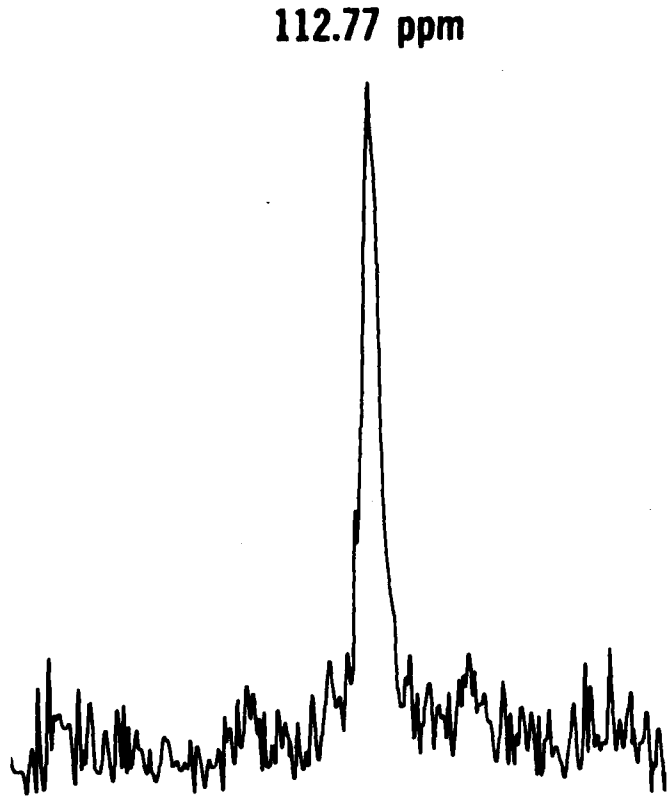

Figure 7. ^{31}P-NMR spectrum of aryl-ZDDP (1A).

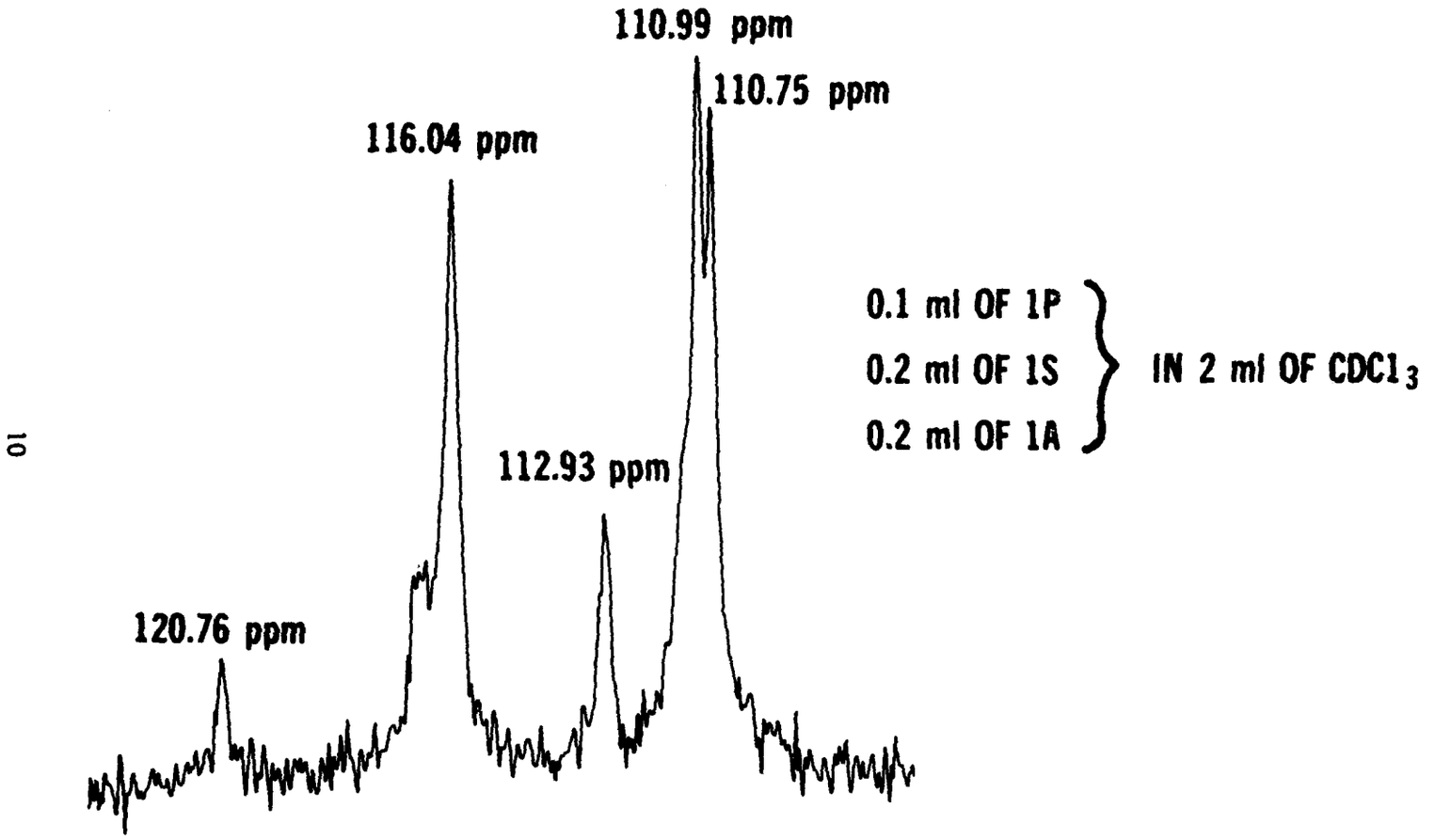

Figure 8. ^{31}P-NMR spectrum of ZDDPs.

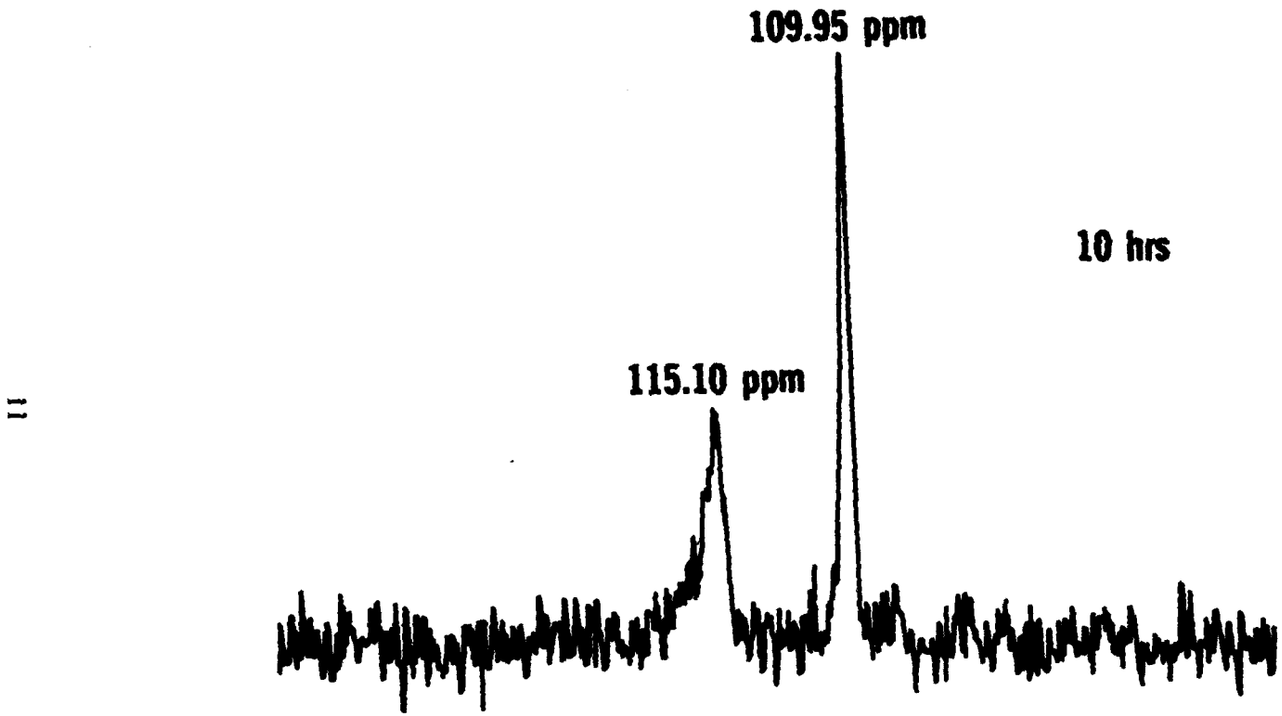

Figure 9. ^{31}P-NMR spectrum of Oil A.

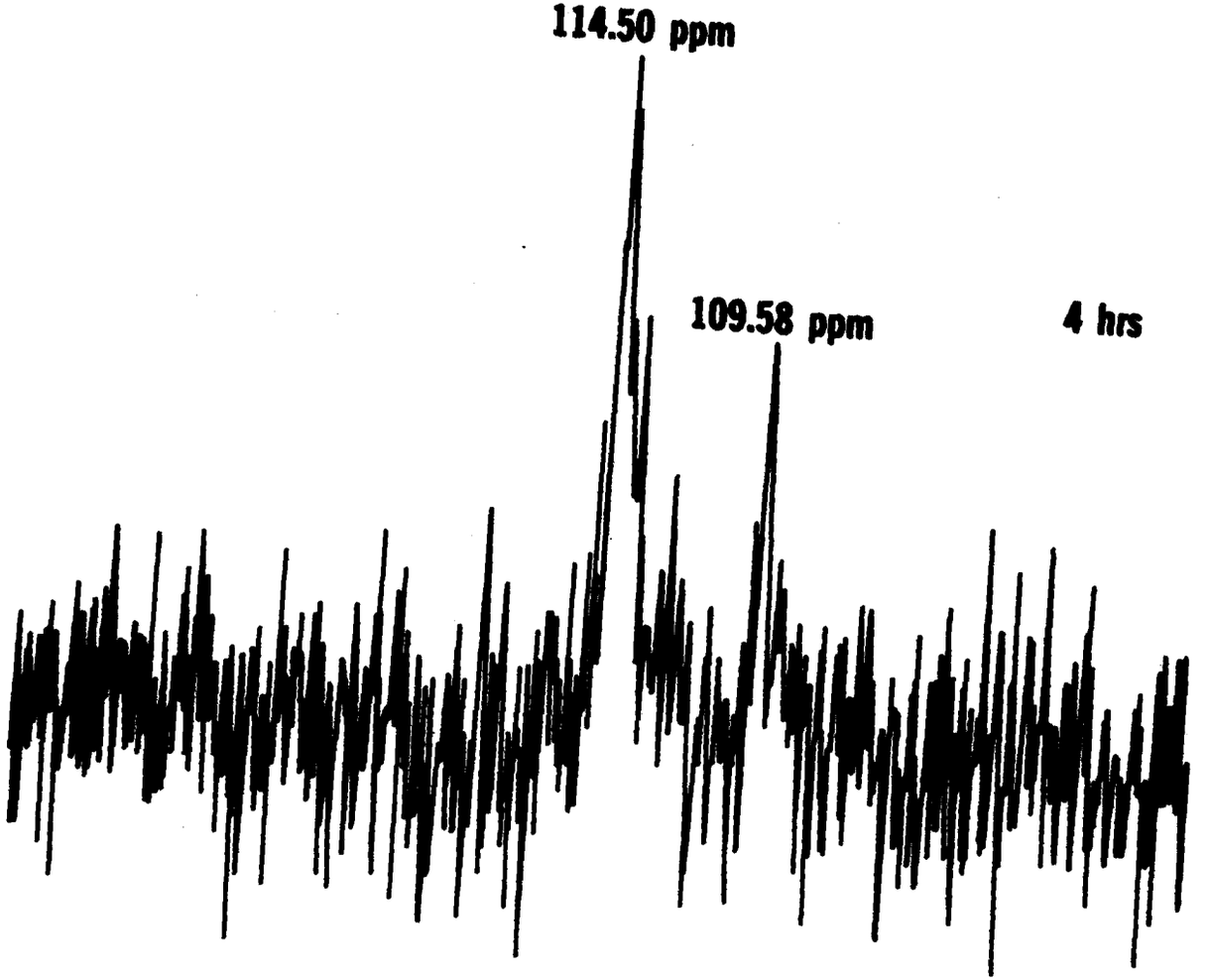

Figure 10. ^{31}P-NMR spectrum of Oil B.

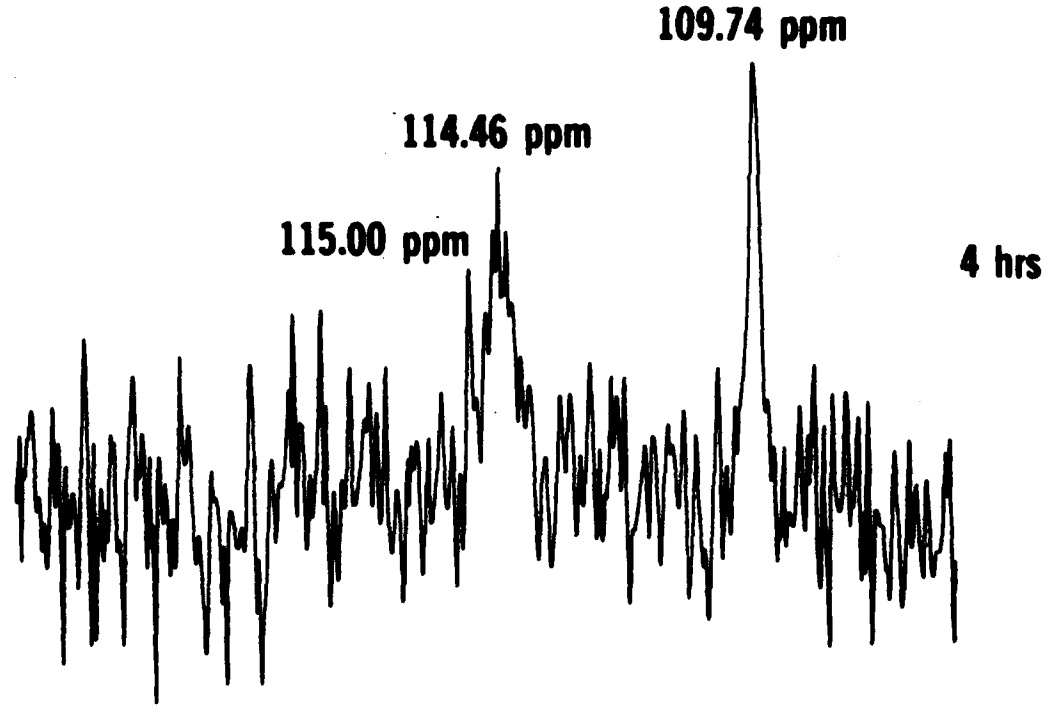

Figure 11. ^{31}P-NMR spectrum of Oil B (18 added).

and 1,3 dimethylbutyl ZDDPs and had α-protons' peaks at 4.88 and 4.78 ppm respectively. The ^{31}P-NMR of 2S showed a single peak at 110.75 ppm and the ^{1}H-NMR spectrum of 2S (Figure 6) showed only one major α-proton of ZDDP and probably was 1,3 dimethylbutyl ZDDP. The ^{31}P-NMR spectrum of 1A (Figure 7) showed only one peak at 112.77 ppm. The ^{1}H-NMR spectrum did not give further information.

The chemical shift in the table clearly shows that the difference of chemical shifts of primary alkyl, secondary alkyl, and aryl ZDDP are large enough to be used for identification. The substitution effects are well established for other nuclei such as carbon-13.[5] This effect is diminished with four bonds or more distance. In other words, the chain length is not the major factor on chemical shift. It is the substitution on α-carbon which will affect the chemical shift. All the ZDDP (1P, 1S or 2S, 1A) are well separated and easy to identify, as shown in Figure 8. The chemical shift of 1P shifted 0.6-0.8 ppm upfield (lower chemical shift from reference TPP) compared to the one shown in the table, while peaks of 1S and 1A remained unshifted. This might be caused by the greater solvent shift of 1P in $CDCl_3$ solvent or carrier oil.

Two Military Specification MIL-L-46152 qualified oils were examined by ^{31}P-NMR. Oil A was reported to contain 0.07% zinc of 1P and 0.07% zinc of 1S. The spectrum of Oil A (Figure 9) gave two peaks at 115.1 and 110.0 ppm with equal amounts (area). But only one peak showed at 110 ppm instead of two peaks as the spectrum of 1S (Figure 4). To examine this result, 1S was added to Oil B which was reported to contain 0.05% zinc of 1S and 0.1% zinc of 1P (Figure 10) providing a final make-up giving ~ 0.1% zinc of 1S.

The resulting spectrum (Figure 11) still showed only one peak at 109.74 ppm as in Figure 9 and Figure 10. Assessment of this spectrum indicated that some type of chemical interaction has occurred between ZDDP and other additives.

The peak area of ^{31}P-NMR spectrum can be used for quantitative analysis since the peak area is in direct proportion to the number of phosphorus molecules. But the area will be affected by spin-lattice relaxation time (T_1) of observing nuclei when using relatively short repetition time. To test this T_1 effect, a 4-s repetition time, which was double that of the typical 2 s used, was employed for each ZDDP and revealed that no noticeable change occurred in peak area. This is the indication of these ZDDPs having short T_1 relaxation time in the order of seconds. A paramagnetic relaxation reagent also can be added to reduce the relaxation time (T_1) of the ^{31}P nuclei and to minimize the T_1 effect.

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[5] G. Levy and G. Nelson, "Carbon-13 Nuclear Magnetic Resonance for Organic Chemists," Wiley-Interscience, New York (1972).

A more systematic examination is needed to establish the optimum experimental conditions. Nuclear Overhauser effect (NOE) also affects the peak area when proton decoupling is employed. As shown in Figure 8, the peak height and area of aryl ZDDP (1A) are much smaller than that of alkyl ZDDP (1P and 1S) after the concentration adjustment. This is expected as the NOE, which is dominated by dipole-dipole interaction, is greater in alkyl ZDDP having protons in three-bond distance than in aryl ZDDP which has protons in four-bond distance.

The precision depends on the concentration of the sample and the number of pulses (scans) for taking the spectrum. For example, the better the signal/noise ratio, the better the precision. The oil-to-solvent ($CDCl_3$) ratio is better, not greater than two. A higher concentrated solution decreased the resolution of spectrum. A minimum concentration of $CDCl_3$ was also required to maintain the lock signal.

2. Infrared (IR) Study. The differential IR spectra of 1P, 1S, 2S, and 1A are shown in Figure 12. The percentage transmission of the spectra was cut by half and recorded. The peak frequencies of alkyl-ZDDP (1P, 1S, and 2S) are quite different from aryl-ZDDP (1A).

The Oil A, which contains equal amounts of 1P and 1S, clearly shows peaks of 1P and 1S at 1000 and 980 cm^{-1}, respectively (Figure 13). Oil B, which contains 0.10% zinc of 1P and 0.05% zinc of 1S, shows only one peak at 1005 cm^{-1} with a shoulder around 980 cm^{-1} (Figure 14). The result shows that a small amount of 1S compared to 1P in the oil is not easily detected and will make quantitative analysis more difficult.

The additive 1S was added to Oil B to make up the concentration of 1S close to the concentration of 1P by the comparison of the IR spectrum (Figure 15) with the spectrum of Oil A (Figure 13). The new oil from Oil B was used for ^{31}P-NMR investigation.

III. EXPERIMENTAL

3. Materials.

a. All the zinc dialkyl(diaryl)dithiophosphate (ZDDP) samples containing a carrier oil were obtained from an additive company:

1P — primary alkyl ZDDP (mixing alkyl, 80%).
1S — secondary alkyl ZDDP (mixing alkyl, 80%).
2S — secondary alkyl ZDDP (one alkyl).
1A — aryl ZDDP (60%).

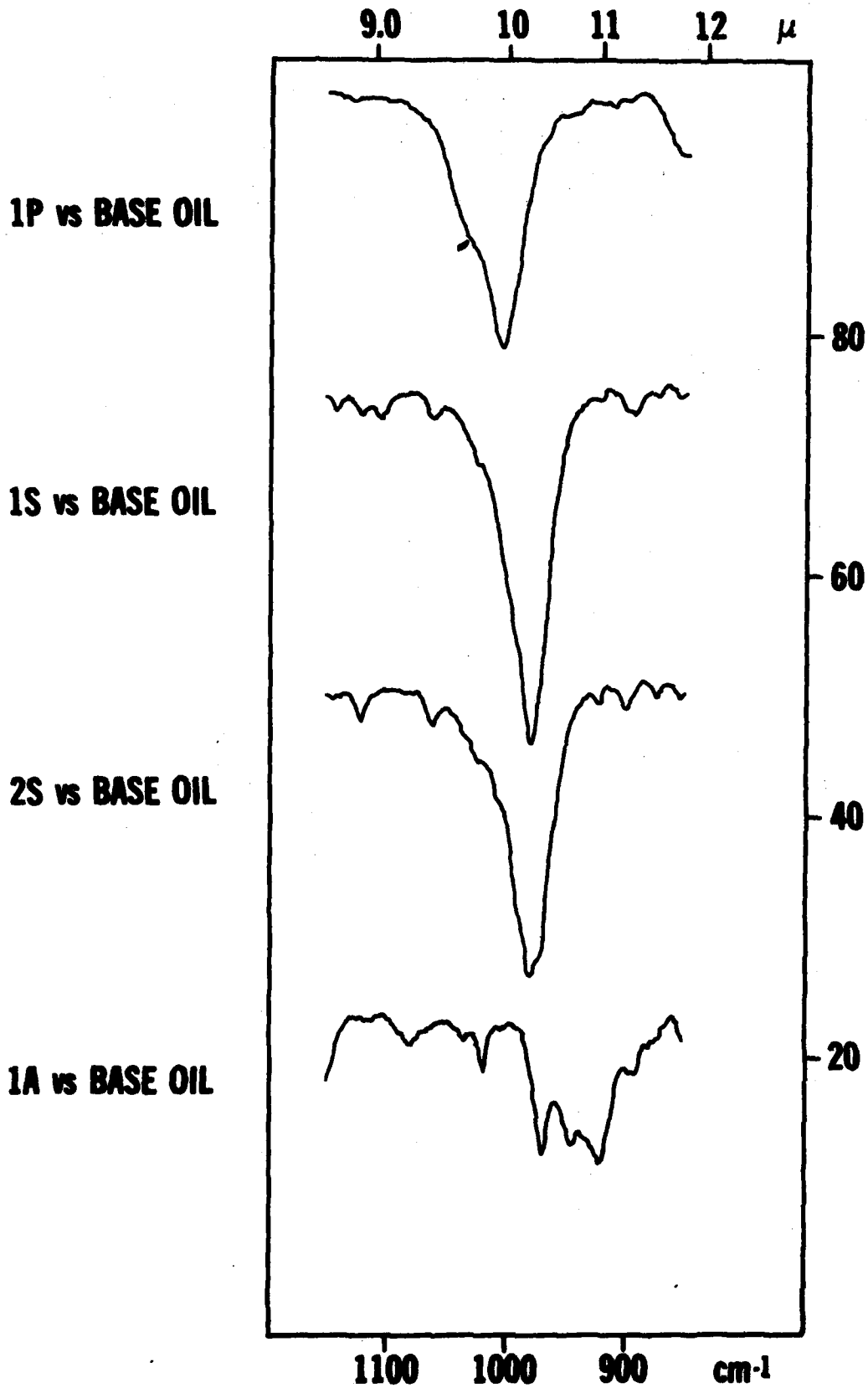

Figure 12. Differential IR spectra of ZDDP additives.

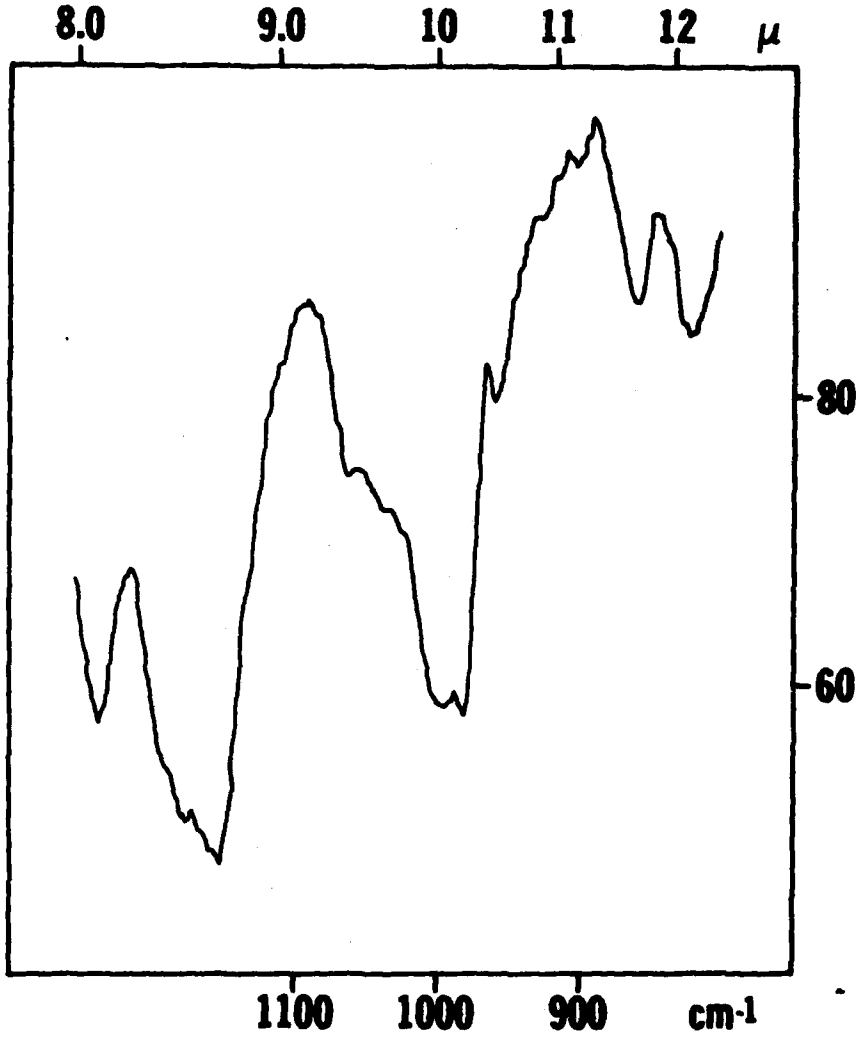

Figure 13. Differential IR spectrum of Oil A vs base oil.

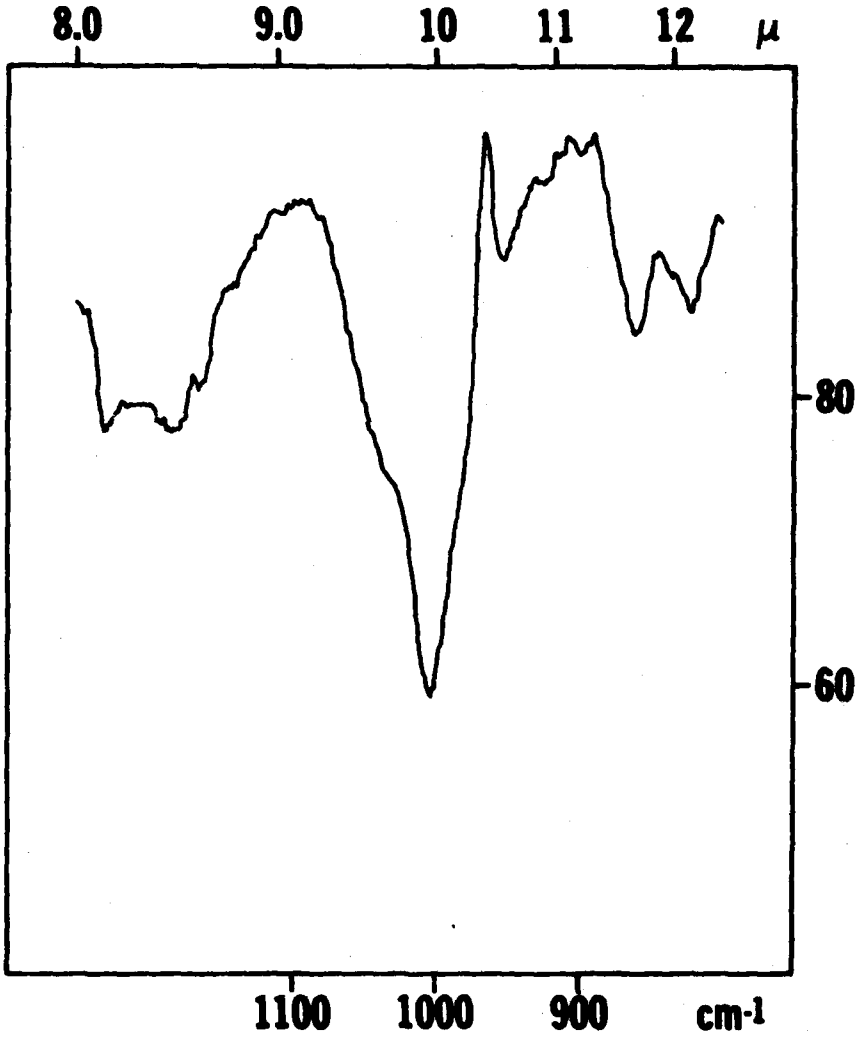

Figure 14. Differential IR spectrum of Oil B vs base oil.

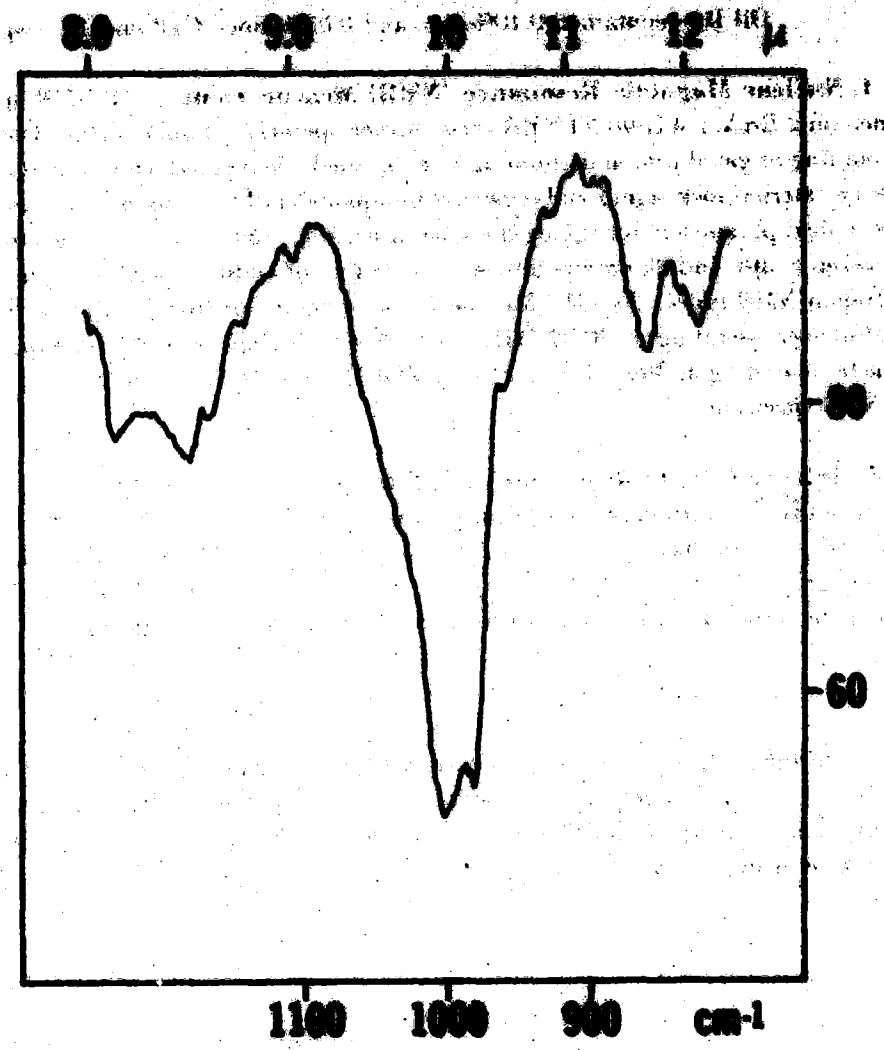

Figure 16. Differential IR spectrum of Oil A (10 added) vs base oil.

b. The finished oils (MIL-L-46152) were taken from retained oil samples which were sent to this laboratory for qualification.

Oil A — contained 0.07% zinc each of 1P and 1S.
Oil B — contained 0.10% zinc and 0.05% zinc of 1P and 1S, respectively.

4. Nuclear Magnetic Resonance (NMR) Measurements. ^{31}P-NMR spectra were obtained on a Bruker WH-90 FTNMR spectrometer operating at 36.44 MHz. Broad-band proton decoupling or gated proton decoupling were applied. Deuterated chloroform was used to provide an internal lock signal and triphenyl phosphate (TPP) was used as an internal reference. The typical parameters for taking the spectra were 5μs (40°) pulses, 2 s repetition time, 6000 Hz sweep width, and 8k data points. A 0.1 to 0.4 ml of additives was added to 2 ml of $CDCl_3$ in 10-mm NMR tubes. The ^{1}H-NMR spectra were obtained either on Bruker WH-90 FTNMR spectrometer operating at 90.02 MHz or on Bruker WH-300 superconducting FTNMR spectrometer operating at 300 MHz. A 1 to 3% ZDDP in $CDCl_3$ in 5-mm NMR tubes was used for ^{1}H-NMR spectrum.

5. Infrared (IR) Measurements. Infrared spectra were obtained on a Perkin-Elmer 580B IR spectrophotometer equipped with PE-3500 data station. A 0.102-mm KBr cell was used. A virgin base stock oil was used as the reference for differential IR. The sample of 1P, 1S, 2S, and 1A was diluted with the same base stock oil 100 times. All spectra reported were differential IR spectra against base stock oil by PE-3500 data station.

IV. CONCLUSIONS

Different types of zinc dialkyl(diaryl)dithiophosphate (ZDDP) in the fully formulated oil can be identified directly by ^{31}P-NMR. The exact structure of alkyl substitution can also be possibly deducted by ^{1}H-NMR after the separation. The quantitative analysis of ZDDP is possible by using ^{31}P-NMR.

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