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Infrared Analysis of Vapor Phase Deposited Tricresylphosphate (TCP)

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Abstract

Infrared transmission was employed to study the formation of a lubricating film deposited on two different substrates at 700°C. The deposit was formed from tricresylphosphate vapors and collected onto a NaCl substrate and on an iron coated NaCl substrate. Analysis of the infrared data suggests that a metal phosphate is formed initially, followed by the formation of organophosphorus polymeric compounds.

Introduction

Tricresylphosphate (TCP) has been used as an antiwear additive in base oils since the early 1900s. It has been concluded (1) that the antiwear effectiveness of TCP results from the formation of a phosphate group on a wearing surface. Recently, TCP has been used in several studies involving the vapor phase lubrication of engineering surfaces at temperatures in excess of 400°C (2-4). In these studies TCP is vaporized into a carrier gas where the gas is directed at a hot surface (metal or ceramic). A deposit is formed on the hot surface over a period of time. In many cases, the resulting deposit was found to be highly lubricious.

Analysis of the resulting deposit has been attempted. Graham and Klaus (2) used SEM to suggest that the deposit exists as a polymer. In a different study, Klaus et al. (5) postulated that the deposit consisted of a bottom layer of Fe_3C and a top layer of Fe_2P, Fe_2C_5, and $FePO_4$. In this present study, infrared analysis of the deposit was performed to characterize more fully the nature of the deposit.

Experimental

The equipment used in this study has been described by Makki and Graham (4). It is basically an oven (Figure 1) where TCP is vaporized into a carrier gas stream and the gas stream is directed to a stationary substrate at a known temperature. Using a syringe pump, liquid TCP is introduced into preheated N_2 carrier gas at a constant rate of 1.6 ml/hr. The TCP concentration was maintained at 1 mole % in the N_2 gas stream flowing at a rate of 200 ml/min. Two different stationary substrates were used: one was a plain NaCl window that is typically used in infrared studies, and the other is a NaCl window that had been coated with approximately 800 Å of iron. Figure 1 shows the dimensions of the substrate. The substrates were maintained at 700 °C.

A time study was then conducted by first exposing a plain NaCl substrate to the TCP vapor stream for 1 minute. A second NaCl substrate was then exposed to the TCP vapor stream for 5 minutes, and finally a third NaCl substrate was exposed to the TCP vapor stream for 10 minutes. This procedure was then repeated for the iron coated NaCl substrates. A transmission infrared analysis was then performed using a Nicolet fourier transform infrared unit.

Results and Discussion

1. Plain NaCl Substrate

Figure 2 is the infrared (IR) spectrum of the 1 minute deposit on a plain NaCl substrate. Analysis of this spectrum suggests that the deposit may be a sodium triphosphate compound with molecular formula $Na_5P_3O_{10}$.. In addition to the triphosphate, a small quantity of an organic compound (or compounds) having a P-O-Ar group may be present. Table 1 lists and compares many of the deposit IR peaks with the known IR peaks of the triphosphate (6). Table 1 also lists the remaining IR peaks with the corresponding group absorptions. Although the 569 cm^{-1} deposit peak could not be adequately assigned, the presence of a Cl compound is a possibility since PCl_2 absorbs in the 590 to 420 cm^{-1} range. KBr powder, containing the pure compound $Na_5P_3O_{10}$, was pressed into a pellet and its FTIR spectrum (Figure 3) was taken. Comparison between figures 2 and 3 shows agreement between nearly all the $Na_5P_3O_{10}$ peaks.

Figure 4 is the IR spectrum of the 5 minute deposit on a plain NaCl substrate. Table 2 lists all the peaks present in three groups. Group I lists the sodium triphosphate compound peaks where all the IR peaks have been diminished or masked by other peaks (due to the apparent formation of a deposit film). Group II lists peaks corresponding to CH, aromatic, and P-O-Ar groups. Many of these peaks are more intense when compared to the 1 minute deposit spectrum. Group 3 lists new peaks that were not present in the 1 minute spectrum. Analysis suggests the presence of P-H, P=O, P-O-P, and P-O-Ar groups. Peaks 1294 cm^{-1}, 1266 cm^{-1}, 992 cm^{-1}, and 693 cm^{-1} are assigned to a pyrophosphate. Only the 640 cm^{-1} and 525 cm^{-1} peaks could not be assigned.

The IR spectrum of the 10 minute deposit on the plain NaCl substrate is shown in Figure 5. Nearly all the IR peaks from the spectrum of the 5 minute deposit are present in the spectrum of the 10 minute deposit. The only major difference in these peaks is that the 10 minute deposite spectrum exhibits much stronger absorptions (possibly due to the growth of the deposit film). The major differences between the 10 and 5 minute deposits are the appearance of the broad peak at about 2880 cm^{-1}, and the sharp peak at 771 cm^{-1}. The broad peak at 2880 cm^{-1} can be attributed to P-O-H absorption and the peak at 771 cm^{-1} to P-O-Ar or P-O-C absorption. The final difference between the 5 and 10 minute deposits is the severe spectral overlap in the C-H region, prohibiting the detection of any C-H absorption after the 10 minute deposit. These results indicate that the initial formation of sodium triphosphate $Na_5P_3O_{10}$ is followed by the appearance of an organophosphorus compound (or compounds) containing P-O-Ar groups. As time progresses, the chemical composition of the deposit apparently changes to include P-H, P=O, and P-O-P groups in addition to the P-O-Ar groups.

2. Iron-Coated NaCl Substrate

One will notice that the legends and format of the IR spectra shown in Figures 6, 7, and 9 are different from previous IR spectra. Unfortunately, the FTIR unit that was being used broke down and this necessitated the use of a different FTIR unit, thus the different formats.

Figure 6 is the IR spectrum of the 1 minute deposit formed on the Fe coated substrate. These peaks are not as well defined nor as sharp as the IR peaks found in the plain NaCl substrates. This is most likely due to the reduced amount of IR radiation transmitted through the Fe coated substrate. Analysis of this IR spectrum suggests the presence of iron phosphate, $FePO_4 \cdot 2H_2O$(6). Table 3 lists and compares the deposit IR peaks with the IR peaks of $FePO_4 \cdot 2H_2O$. In addition to the iron phosphate an organic phosphorous material may be present. Table 3 also lists these peaks. Peaks 2957 cm^{-1}, 2911 cm^{-1}, and 2846 cm^{-1} result from C-H absorptions. Peaks 982 cm^{-1} and 906 cm^{-1} can also be attributed to P-O, P-O-C, or P-O-P absorptions (ref. 7). Peak 1034 cm^{-1} can be attributed to P-O-C absorption. KBr powder, containing the pure compound $FePO_4 \bullet 2H_2O$, was pressed into a pellet and its FTIR spectrum (Figure 7) was taken. Comparison between figures 6 and 7 shows agreement between the major peak assignments of $FePO_4 \bullet 2H_2O$.

Figure 8 is the IR spectrum of the five minute deposit. Comparison with the one minute deposit shows the presence of four new peaks: at 1266 cm^{-1}, 1089 cm^{-1}, 1017 cm^{-1}, and 770 cm^{-1}. The iron phosphate peaks are no longer detectable (due to the formation of a deposit film). Peaks 1266 cm^{-1} and 1089 cm^{-1} can be attributed to P=O absorption whereas peak 1017 cm^{-1} can result from P-O-C absorption. Peak 770 cm^{-1} can be attributed to P-O-C or P-O-Ar absorption. The C-H peaks at 2957 cm^{-1}, 2911 cm^{-1}, and 2846 cm^{-1} are still present and appear to be stronger.

Figure 9 is the IR spectrum of the ten minute deposit on the iron coated substrate. Comparison with the five minute deposit reveals no new peaks. The only difference is stronger absorption of the peaks at 1089 cm^{-1}, 1017 cm^{-1} and the doublet at 770 cm^{-1}.

These results indicate that $FePO_4 \cdot 2H_2O$ is initially formed on the iron (iron oxide) coated NaCl substrate. This is followed by the appearance of a possible organophosphorus compound (or compounds) having C-H, P-O-C, and possible P-O-P groups. The deposit grows, covering the suspected iron phosphate layer, and now may consist of C-H, P=O, P-O-C, and P-O-P groups.

Conclusions

Analysis of the infrared spectra indicates that the initial product formed, from TCP, on the stationary hot substrates is a metal phosphate (sodium triphosphate or iron phosphate). The metal phosphate apparently then serves as an "active" surface for the formation and growth of possible organophosphorus compounds. The growth of the deposit could be polymeric in nature; thus, this work supports the suggestion made by Graham and Klaus.

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Table 1
1 Minute Deposit, Plain NaCl

Peaks Observed (cm^{-1})	$Na_5P_3O_{10}$ Peaks (cm^{-1})
~1656 → 1606	~1620 w, vb
--	1265 w
1215	1215 s
1149	1146 vs
1095	1095 s
1031	1022 w
990	989 w
909	912 s,b
--	798 vw,b
754	753 m
733	731 w
712	708 s

Peaks Observed (cm^{-1})	Structural Group Assignment To Observed Peaks (cm^{-1})
≈3356 vb	O-H
3055	C-H
2919	C-H
1606	Aromatic str
1483	Aromatic str
1453	Aromatic str
1407	Aromatic str
1378	—
782	P-O-Ar
618	A-O-Ar
569	PCl_2

Table 2
5 Minute Deposit, Plain NaCl

I $Na_5P_310_{10}$ Peaks Diminished (cm^{-1})

I $Na_5P_310_{10}$ Peaks Diminished (cm^{-1})
~1656
1215
1152
1095
1031
909
782
733

II Peaks Observed (cm^{-1})	Structural Group Assignments To Observed Peaks (cm^{-1})
≈3400	OH
3053	C-H
2965	C-H
2919	C-H
2872	C-H
1606	Aromatic
1484	Aromatic
1454	Aromatic
1400	Aromatic
782	P-O-Ar
617	P-O-Ar

III New Peaks Observed (cm^{-1})	Structural Group Assignments For Observed Peaks (cm^{-1})
2371	P-H
1640	O-H
1294	P=O
1266	P=O
1125	PH, P=O
992	P-O, P-O-P
753	P-O-Ar
693	P-O-P
640	--
525	—

Table 3
1 Minute Deposit on Fe Coated Substrate

Peaks Observed (cm^{-1})	$FePO \bullet 2H_2O$ Peaks (cm^{-1})
~3400 b	~3330 s,b
1625	1600
--	1385
--	1255 vw
1102	1105
1064	1068
1005	1005
--	850

Peaks Observed (cm^{-1})	Structural Group Assignment To Observed Peaks (cm^{-1})
2957	
2911	C-H
2846	C-H
1184	C-H
1034	--
982	P-O-C
906	P-O, P-O-C, P-O-P
	P-O, P-O-C, P-O-P

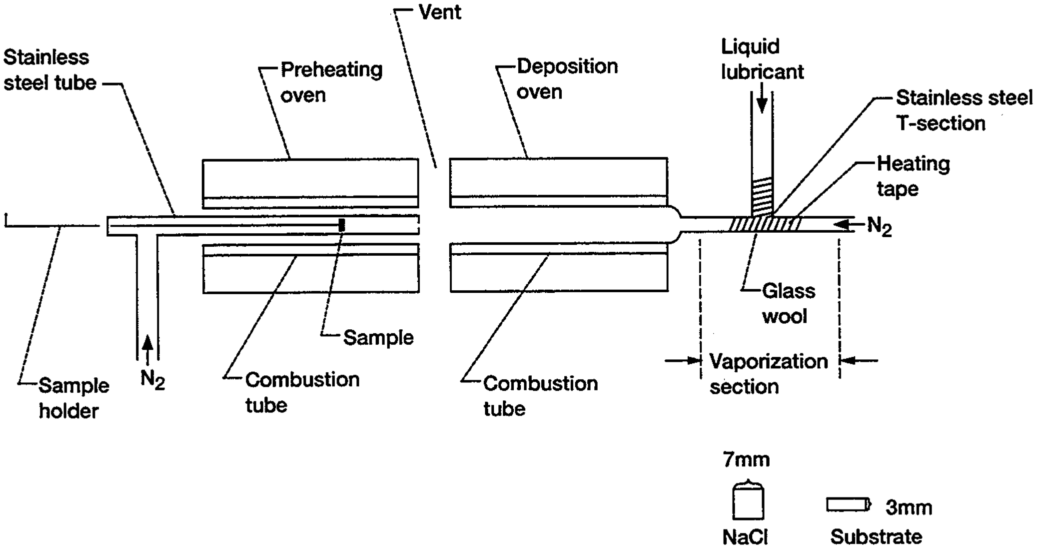

Figure 1.—Apparatus for vapor phase lubrication of stationary samples.

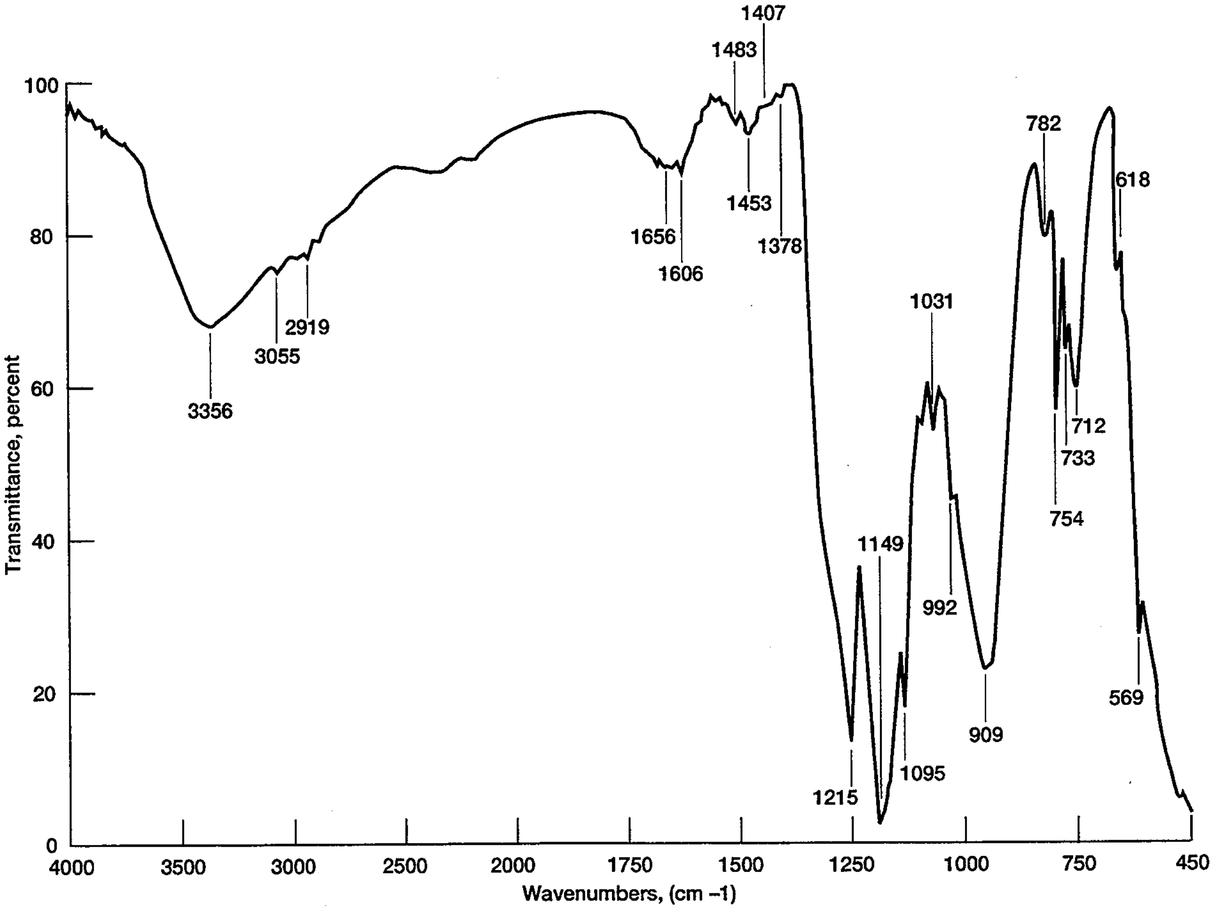

Figure 2.—Infrared spectrum of 1 minute deposit. TCP on plain NaCl substrate.

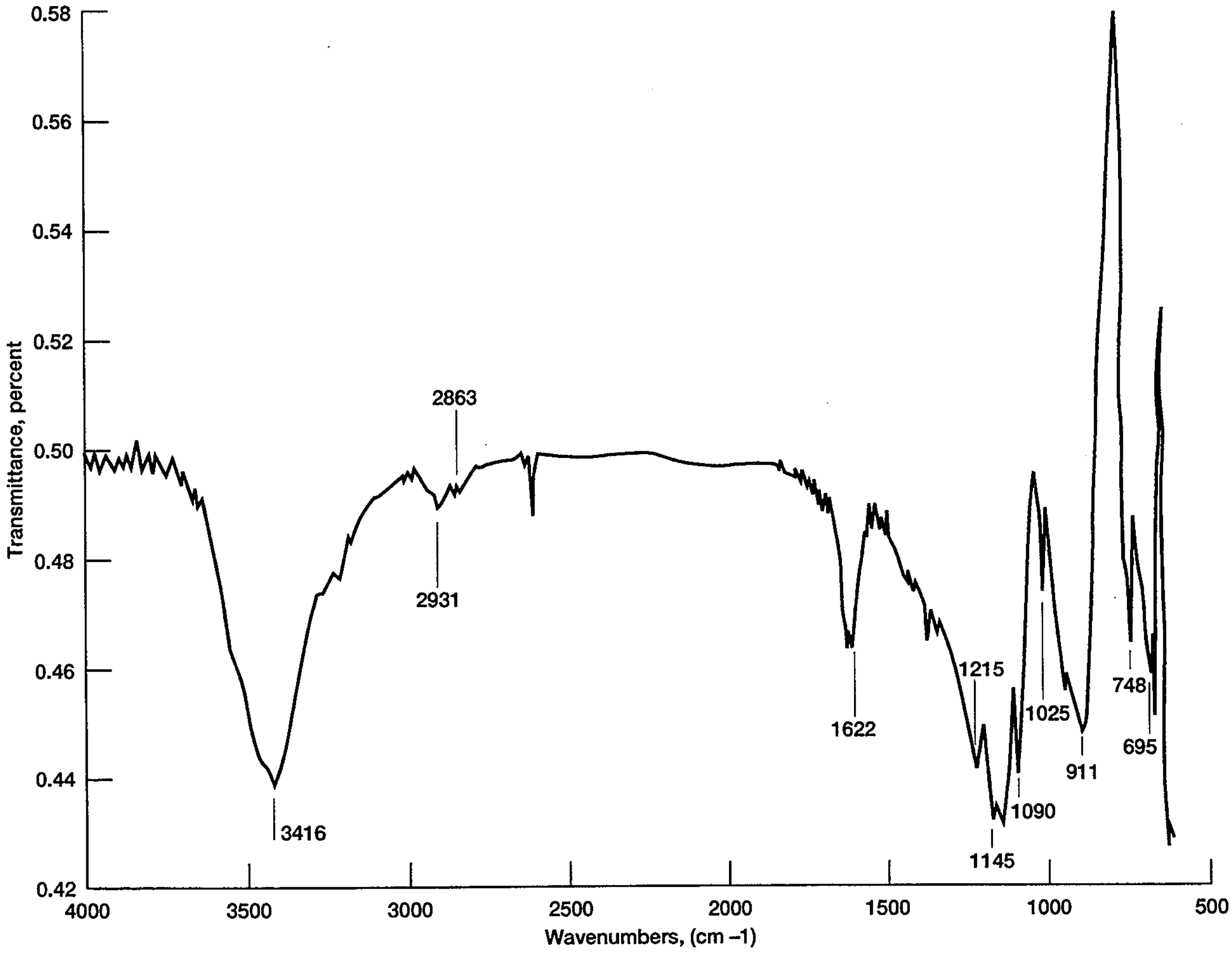

Figure 3.—Infrared spectrum of pure $Na_5P_3O_{10}$.

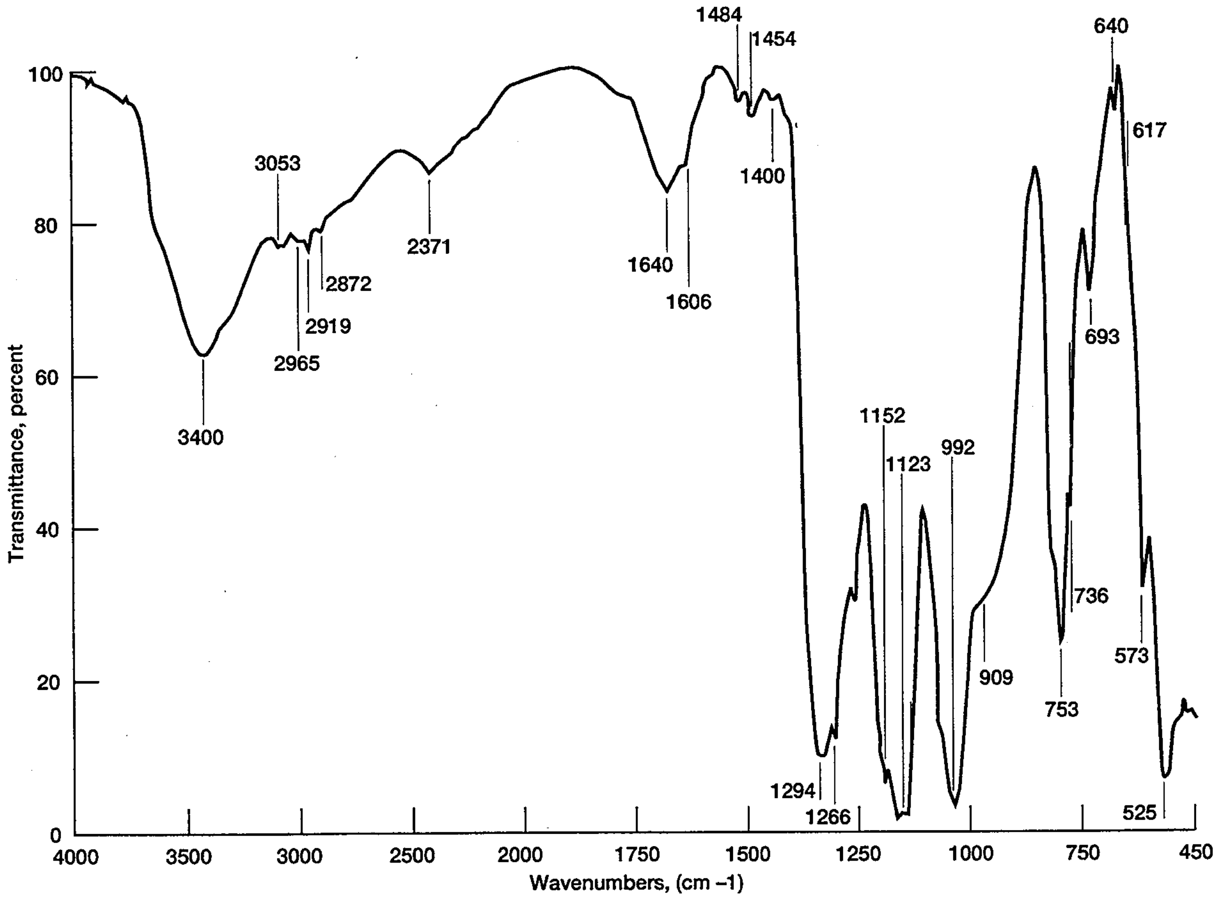

Figure 4.—Infrared spectrum of 5 minute deposit. TCP on plain NaCl substrate.

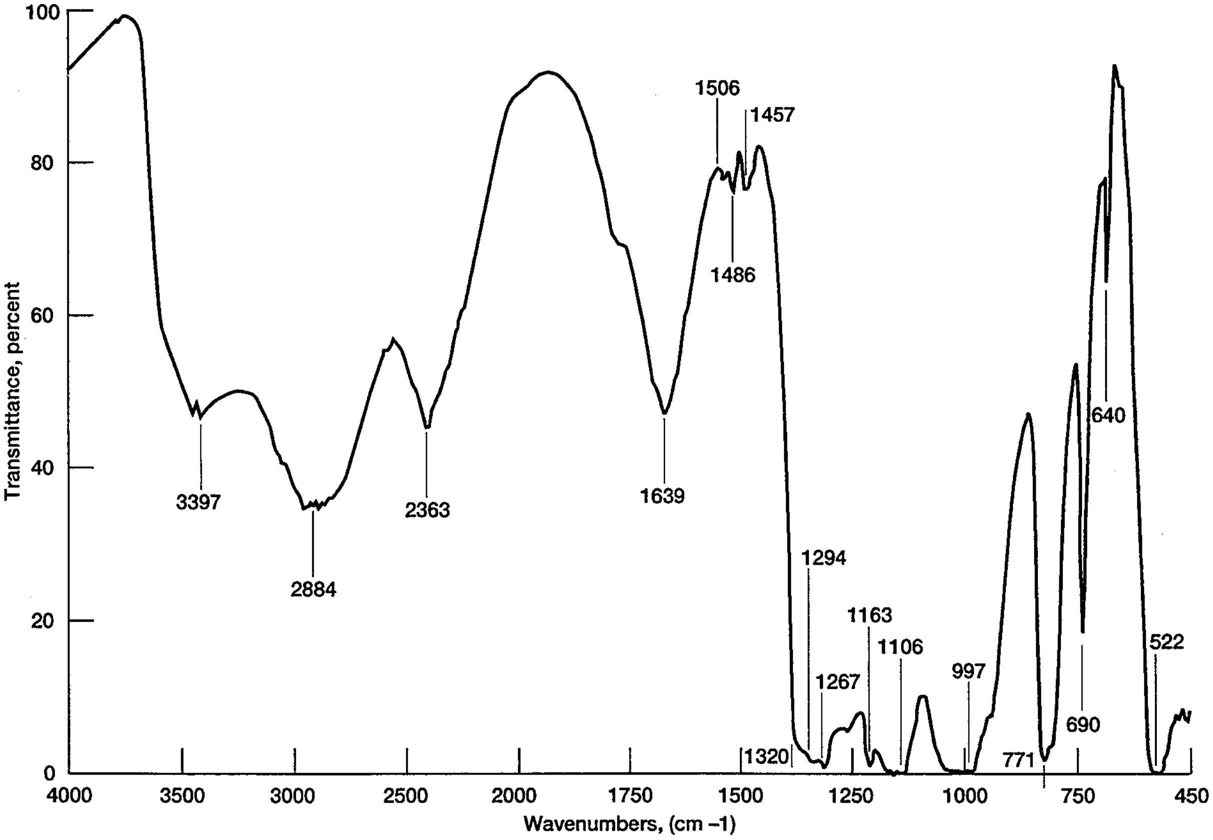

Figure 5.—Infrared spectrum of 10 minute deposit. TCP on plain NaCl substrate.

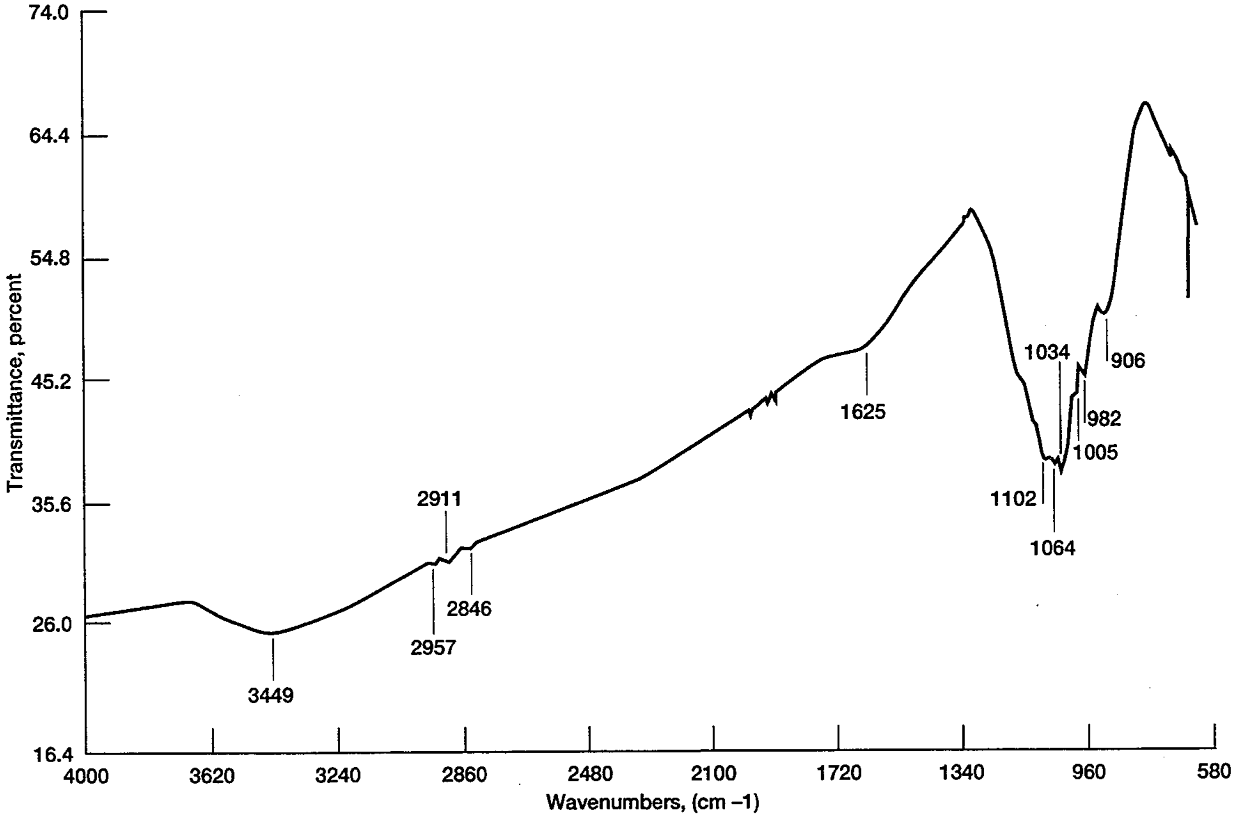

Figure 6.—Infrared spectrum of 1 minute deposit. TCP on Fe coated NaCl substrate.

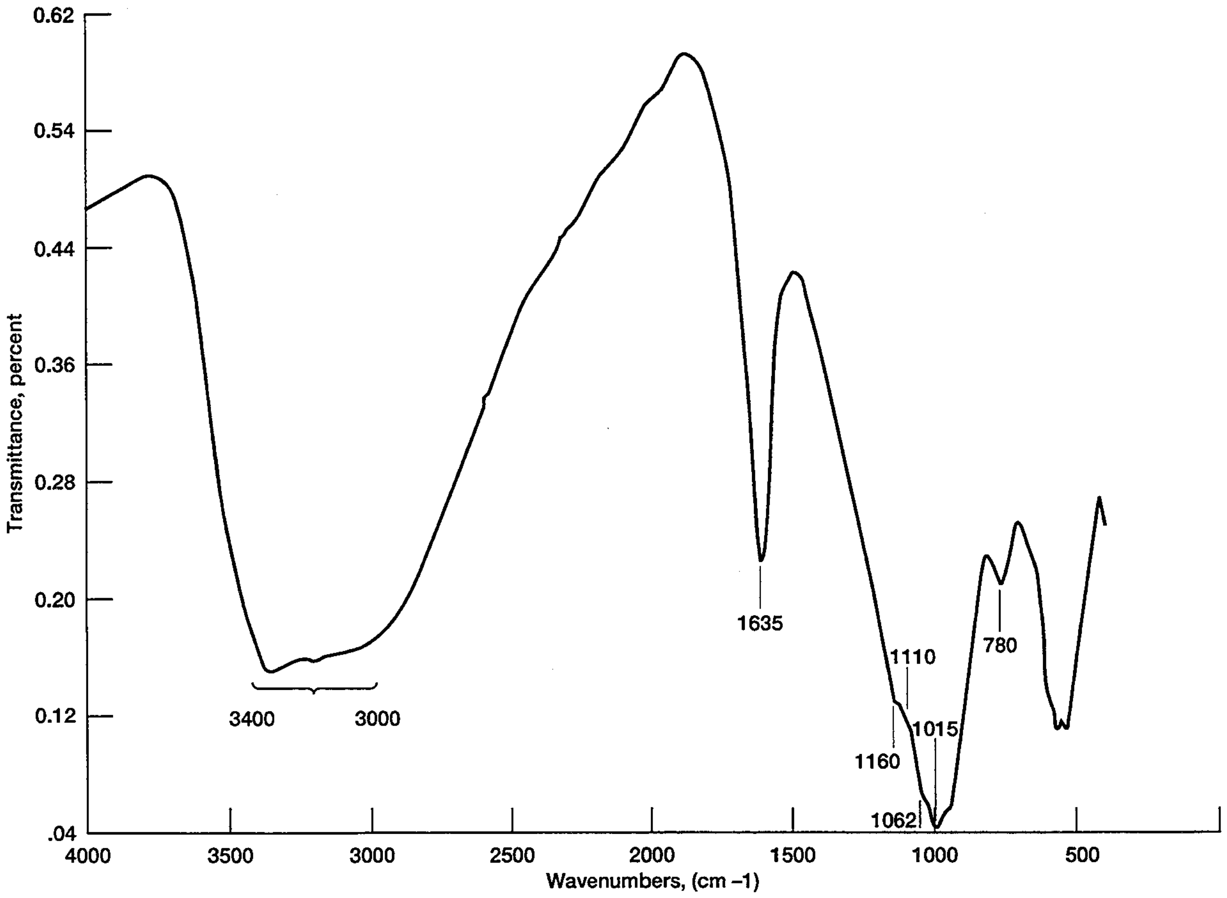

Figure 7.—Infrared spectrum of pure $FePO_4 \cdot 2H_2O$.

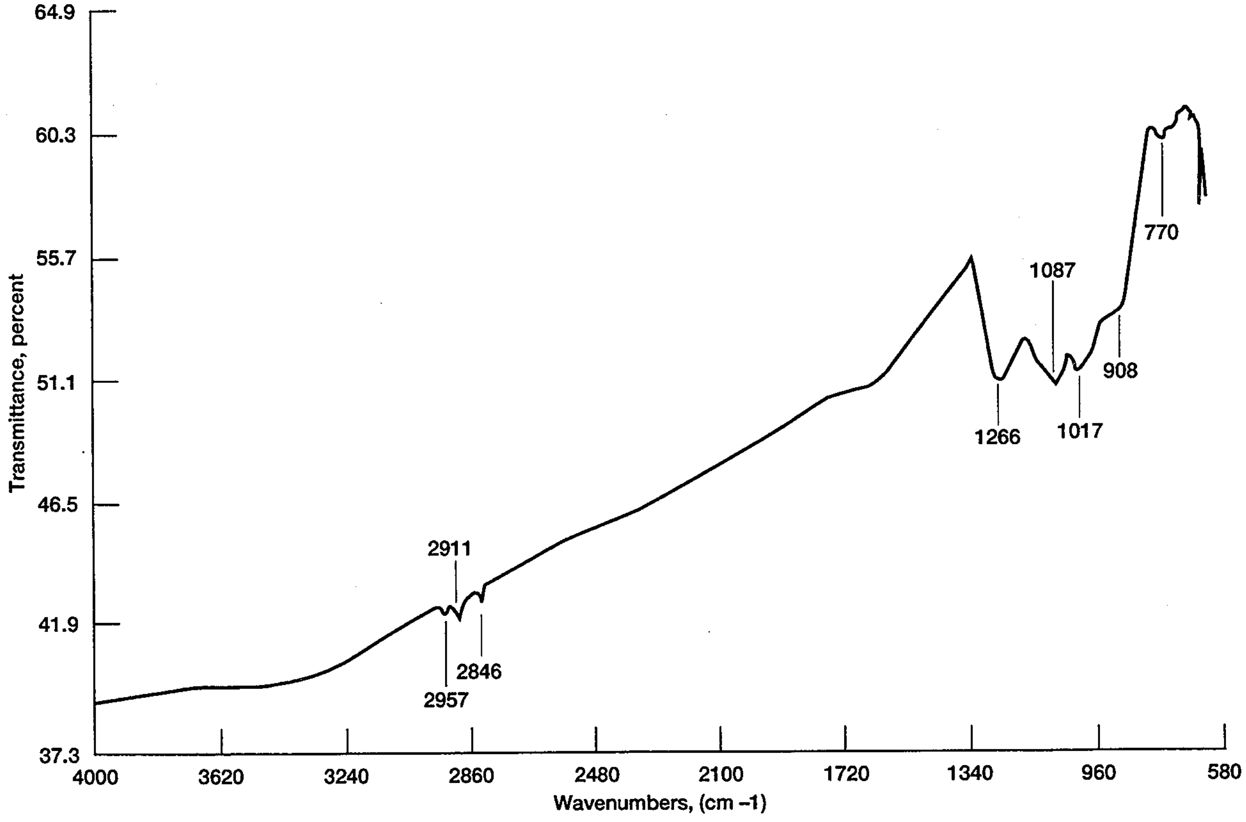

Figure 8.—Infrared spectrum of 5 minute deposit. TCP on Fe coated NaCl substrate.

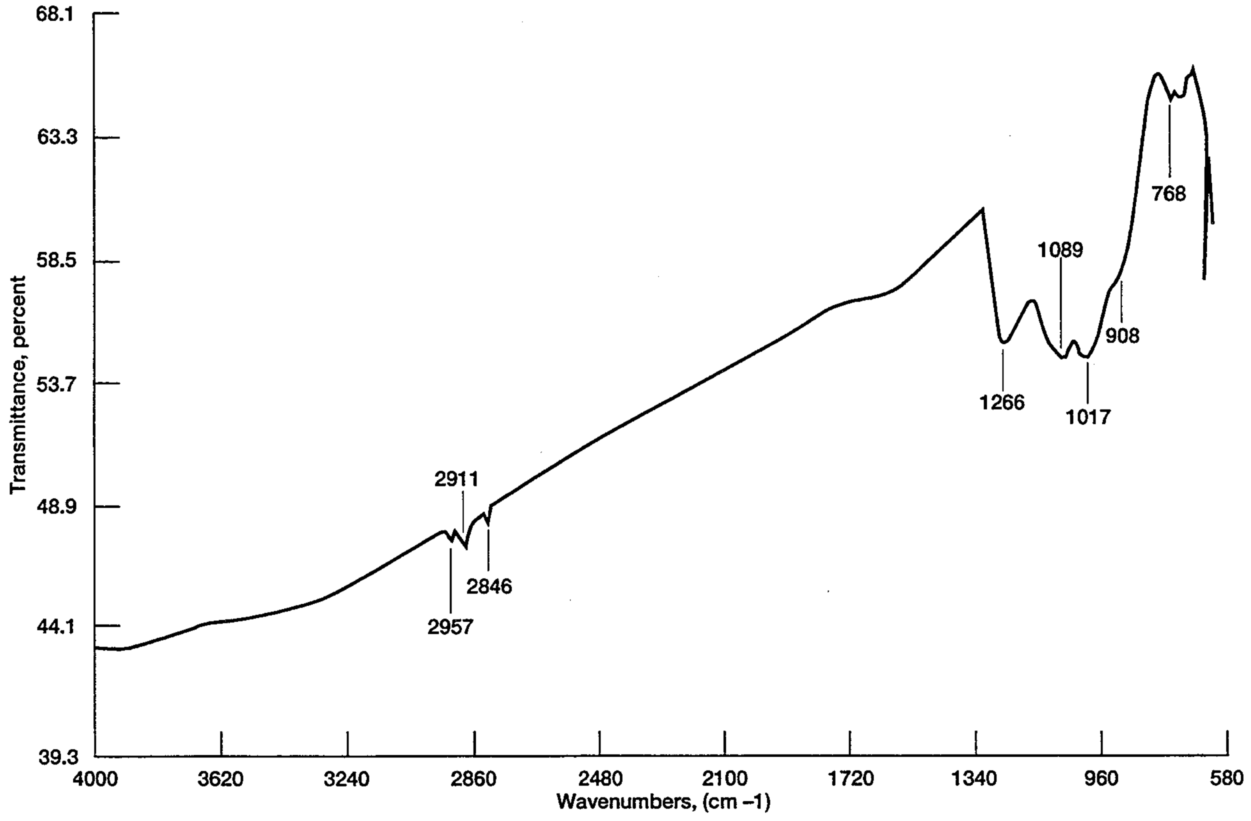

Figure 9.—Infrared spectrum of 10 minute deposit. TCP on Fe coated NaCl substrate.

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13. ABSTRACT ***(Maximum 200 words)***

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