Chapter V

Mannich bases and phosphosulphurized Mannich bases: synthesis, characterization and performance evaluation as potential lube oil additives

2.5.1 Introduction

Base fluids oil generally cannot satisfy the requirements of high performance lubricants without addition of modern additives. Additives are synthetic chemical substances that can improve the different properties of lubricants. The development of modern engine and transmission technologies would have been impossible without modern lubricant additives chemistry and lubricant formulation. Modern engine oil contains a wide range of additives, which are blended with base oil to form a complete package capable of meeting demanding performance [1.] The functions of lubrication additives include improvement of the viscosity index,[2] pour point,[3] oxidative or thermal stability,[4] anti wear performance[5] of the base oil, to minimize rust and corrosion,[6] to lessen the deposition of harmful chemicals on lubricated parts and so on.[7] Dispersant additive contains a polar head group with an oil soluble hydrocarbon tail, keeps metal surfaces clean by preventing deposition of oxidation products of internal combustion engines.[8-10] The mechanism of dispersancy is generally described on the basis of adsorption of the additive through its polar ends on the sludge materials.[11, 12] Detergent additives generally neutralize acidic products which are formed during oxidation of lube oil and thereby minimize corrosion, rust and deposit formulation in the engine. Detergents additives also act to prevent the deposition of sludge in the engine. They are an integral part of any engine oil formulation and are typically metal salt of organic acid, containing a surface active polar group which can react with the metal surface to form a protective film that keeps the metal surfaces of an engine clean.[13] The main functions of detergents in engine oils are acid neutralisation, oxidation inhibition and rust prevention. These functions provide engine cleanliness and extended trouble free operation.[14] The most important mode of lubricant degradation is oxidation. Due to oxidation, there is increase of kinematic viscosity, pour point, sludge of lube oil and enhanced engine corrosion. Additives that reduce the oil oxidation are called antioxidants, which act to retard oxidation of lubricating oil, thus preventing the formation of corrosive products. Antioxidants act in two different ways, by inhibition of peroxides or as radical scavengers', which react with peroxy radicals, thus preventing further propagation of the free radical chain. Peroxide inhibitors react with hydro peroxide molecules preventing the peroxy radical oxidation resulting from high temperature. That may change the chemical structure of the base oil.[15] Generally; all types of base oil should contain some antioxidants depending on the amount of unsaturation and natural inhibition present. The refined mineral base oils contain natural inhibitors in the form of sulphur and nitrogen compounds for much application.[16, 17]

In the present work, three Mannich bases were prepared by using P-Cresol, formaldehyde and different amines (ethylenediamine, diethylenetriamine and triethylenetetramine) and finally the Mannich bases were treated with P_2S_5 to synthesize another three phosphosulphurized Mannich bases. The efficiencies of the prepared compounds were investigated as antioxidant, detergent/dispersant, viscosity modifier and pour point depressant additive for lube oil but it was found that the prepared additives cannot improve the viscosity index and pour point depressant property of lube oil. Therefore, our study was directed for the study of antioxidant and detergent/dispersant properties of lube oil.

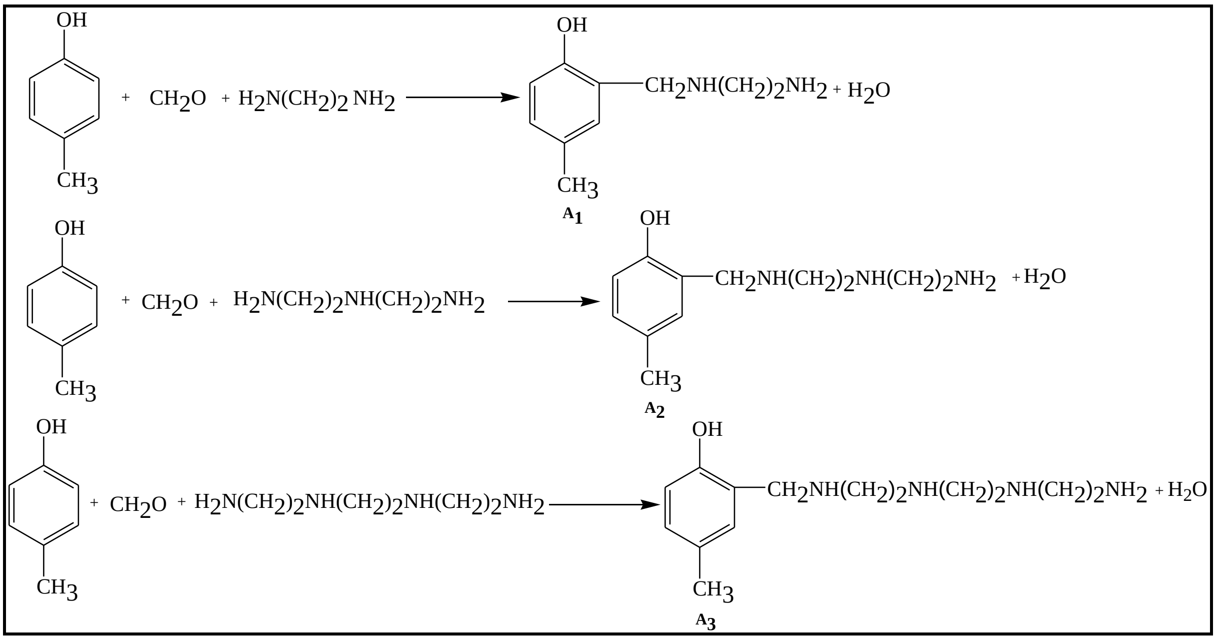
2.5.2 Experimental section

2.5.2.1 Chemicals used

P-Cresol (GC, 98%) was purchased from Thomas Baker (Chemicals) Pvt. Ltd. Formaldehyde (37% w/v) was collected from Sd. Fine Chem. Ltd. and used without any purification. Ethylenediamine (99%, SRL), diethylenetriamine (GC 97%, Sd. Fine Chem. Ltd), triethylenetetramine (GC 98%, LOBA Cheme) and Phosphorous pentasulphide (GC 98%, Sd. Fine Chem. Ltd) were used without any further purification. Benzene (Thomas Baker, 95%) and methanol (Thomas Baker, 98%) were used after purification by distillation method. Base oil was collected from IOCL, India. Properties of base oil are given in table **2.5.1**.

2.5.2.2 Preparation of Mannich bases

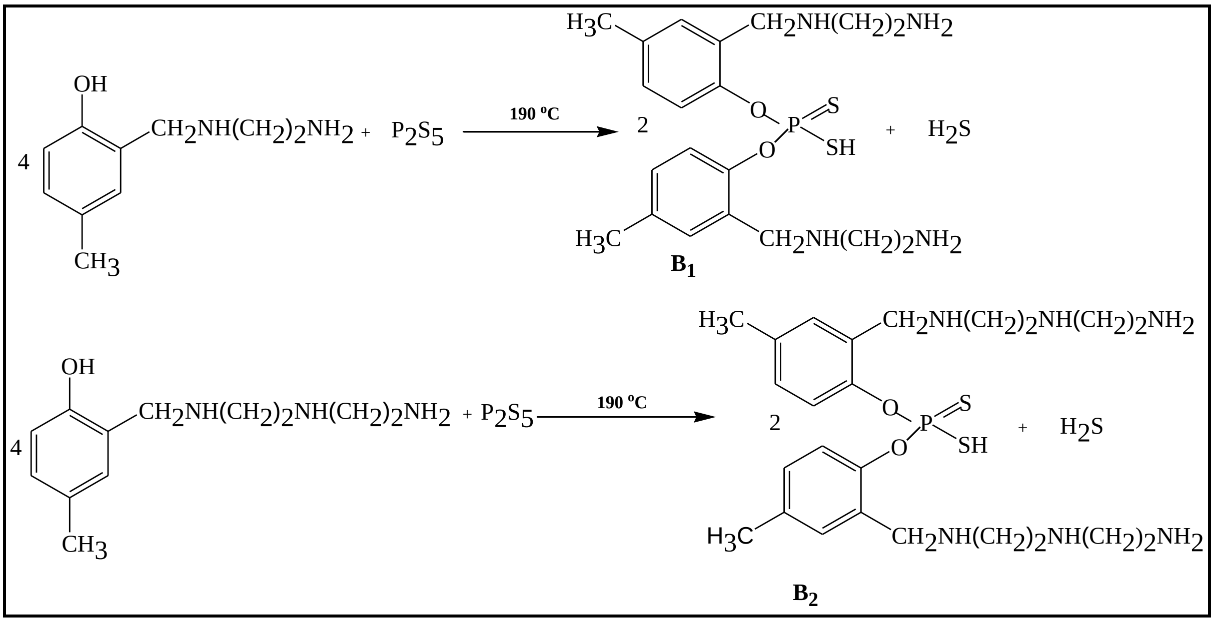
In a 5 necked round bottom flask, fitted with a mechanical stirrer, a ground joint thermometer, a condenser and a dropping funnel, the appropriate amount of p-cresol in methanol and aqueous solution of polyethylene polyamines were added. A formaldehyde (37%) solution was added drop wise during 1 hour at room temperature under nitrogen atmosphere. When the addition of formaldehyde is completed, the temperature of the mixture was raised to reflux temperature for 3 hour. The mixture was then cooled to room temperature. The upper layer was separated from the lower viscous layer (product). The product was dissolved in benzene and washed three times with distilled water to remove the excess of amine and formaldehyde. The molar ratio of p-cresol, formaldehyde and polyethylene polyamines were taken as 1:1:1 ratio. The prepared three Mannich bases with ethylenediamine, diethylenetriamine and triethylenetetramine have been designated by A_1, A_2 and A_3 respectively.

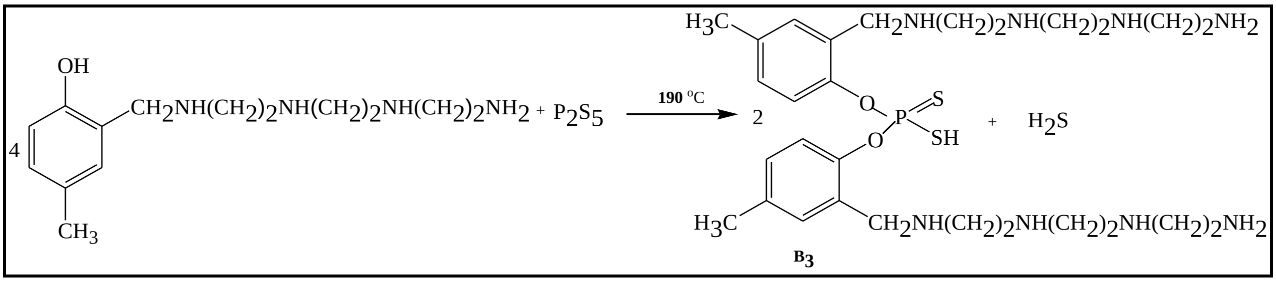


Scheme 1 Preparation of three Mannich bases A_1, A_2 and A_3

2.5.2.3 Preparation of phosphosulphurized Mannich Bases

A four necked round bottom flask, fitted with a mechanical stirrer, thermometer, condenser and inlet for passing nitrogen gas was used for the reaction. The reactions were carried out with four moles of prepared Mannich bases and one mole of P_2S_5 in methanol. The reaction mixture was maintained at 190 ^{0} C with continuous stirring for 4 hour. Three products of phosphosulphurized Mannich bases have been prepared using three Mannich bases to give B_1, B_2 and B_3 respectively.





Scheme 2 Preparation of three phosphosulphurized Mannich bases B_1, B_2 and B_3

2.5.3 Measurements

2.5.3.1 Spectroscopic measurements

IR spectra were recorded on a Shimadzu FT-IR 8300 spectrometer using 0.1mm KBr cells at room temperature within the wave number range of 400 to 4000 cm $^{-1}$. NMR spectra were recorded in Bruker Avance 300 MHz FT-NMR spectrometer using a 5 mm BBO probe. $CDCl_3$ was used as solvent and tetramethylsilane (TMS) as reference material.

2.5.3.2 Determination of the molecular weight

The mean molecular weight of the prepared six additives was determined by using Gel Permeation Chromatography (GPC, Model number-waters 2414). In this method, the samples were dissolved in HPLC grade THF (0.4%, w/v) (used as mobile phase) in the Water GPC system (polystyrene calibration) at 35 ^{0}C at a flow rate of 1ml/min.

2.5.4 Performance evaluation of the prepared compounds as lube oil additives

2.5.4.1 As antioxidant

The lube oil sample and its blends containing 3% additive by weight of each of the prepared additives were subjected to severe oxidation condition in presence of copper and iron strips at 165.5 ^{o} C for 72 hours using Indiana test method of oxidation.[18] The oxidation stabilities of the lube oil blends is expressed in terms of variation of viscosity ratio and change in total acid number and it was determined by taking samples at intervals of 24 hour and up to 72 hour of oxidation and the samples were tested for:

2.5.4.1.1 Variation of viscosity ratio (V/V_o)

The variation of viscosity ratio was determined using Ostwald Viscometer (size 200, No 3205) using ASTM D-2270 method, where V= Kinematic viscosity at 40^{o}C of sample after oxidation, V_o = Kinematic viscosity at 40 ^{o} C of sample before oxidation.

2.5.4.1.2 Change in total acid number (ΔT.A.N)

The total acid number (TAN) is a measurement of acidity that is determined by the amount of KOH in milligrams that is needed to neutralize the acids in one gram of oxidized oil sample. The change in total acid number was calculated according to ASTM D 664-95 standard test method where ΔT.A.N = total acid number of sample after oxidation – total acid number of sample before oxidation.

2.5.4.2 As dispersant

Spot method was applied to determine dispersancy.[19] A few drops of oxidized product of pure lube oil and lube oil containing 3% additive (w/w) were taken from the Indiana oxidation apparatus where samples are oxidized at 165.5 ^{o} C in presence of Fe and Cu strips and after each 24 h intervals of oxidation and up to 72 h to make spots on filter paper (Durieux 122) and dispersancy of the sample were measured as follows:

$$\% \text{ Dispersancy} = \frac{\text{Diameter of the black spot}}{\text{Diameter of the total spot}} \times 100$$

The efficiency of dispersants has been classified as follows:

Up to 30% no dispersancy, 30-50% medium dispersancy, 50-60% good dispersancy
60-70% very good dispersancy, Above 70% excellent dispersancy.

2.5.5 Results and discussion

2.5.51 Determination of molecular weight

The molecular weight of the prepared Mannich bases and Phosphosulphurized Mannich bases were determined by GPC and it is observed that there is no much difference between experimental and theoretical molecular weights. The molecular weight values are depicted in **table 2.5.2**.

2.5.5.2 Spectroscopic data analysis

IR spectrum of prepared Mannich bases: The –NH and –OH group regions are overlapping in the range of 3600-3200 cm $^{-1}$. Peak for the presence of C-N linkage appeared at 1250 cm $^{-1}$ and 1103cm $^{-1}$. Disappearance of –CHO group range of 1720-1740 cm $^{-1}$ and appearance of benzylic –CH_2 in the range of 2850-3000 cm $^{-1}$ indicate that completion of the reaction. In case of ^{1}H-NMR, the disappearance of –CHO proton peak at δ 9.92 ppm and appearance of benzylic - CH_2 peak at δ 3.8 ppm supports the IR observation. ^{13}C NMR also confirms the formation of benzylic –CH_2 proton, (appearance of peak at δ 47 ppm) (**figures 2.5.1, 2.5.2 and 2.5.3**).

The IR peaks at 2360-2372 cm $^{-1}$ (-SH group), 1018-1040 cm $^{-1}$ (P-O bond), 686.6 cm $^{-1}$, 625 cm $^{-1}$ and at 455-463 cm $^{-1}$ (P=S bond) and in the range 1100 – 1040 cm $^{-1}$ (Ar-O bonds) indicate the formation of phosphosulphurized Mannich bases B_1, B_2 and B_3 (**figures 2.5.4, 2.5.5 and 2.5.6**).

2.5.6 Performance analysis of Mannich bases

The prepared compounds A_1, A_2 and A_3 were added to the lube oil samples and the oxidation stability as well as detergency/ dispersancy of all samples under evaluation were determined and compared with lube oil sample without any additives.

2.5.6.1 As antioxidant

The prepared Mannich bases A_1, A_2 and A_3 were added to the lube oil samples in 3% concentration by weight and the blends were subjected to severe oxidation condition as described in experimental section. The oxidation stability is expressed in terms of increase in kinematic viscosity ratio (v/v_0), and change in total acid number (ΔT.A.N), compared with lube oil samples free from additives. Results are given in **figures 2.5.7** and **2.5.8**, which indicate the followings:

The additives A_1, A_2 and A_3 exert better oxidation resistance properties to the additive doped lube oil than the additive free oil. It may be due to the presence of phenolic or amino groups in their structures, which act as chain breaking inhibitors (antioxidants) by donation of labile hydrogen from groups (-OH or –NH) to stabilize the chain radicals; i.e., these inhibitors destroy the peroxide radicals and thus, the oxidation chain is broken.[20, 21] The presence of amine part present in the prepared Mannich bases neutralizes some of the acidic products formed during oxidation. The kinematic viscosity ratio (V/V_0) and total acid number change (ΔT.A.N) decrease with increasing the number of –NH groups present in the amines used. The performances of the additives follow the order $A_3 > A_2 > A_1$.

2.5.6.2 As dispersant/ detergent

The base oil with 3% (w/w) additives were subjected to severe oxidation conditions using the Indiana test method as described in experimental section, in which the efficiency of the dispersant additive increases the diameter of the black spot. This is due to the enhanced capability of the doped oil to carry the oxidation products to a longer distance from the centre of the spot. It may be due to the fact that the –NH groups form hydrogen bonds with the polar end of alcohol, aldehyde, ketone, acids etc which are formed during oxidation.[22, 23] The values of dispersants are given in **table 2.5.3**. From the data, it is clear that dispersancy increases with increasing the number of –NH groups present in the prepared additive. The highest dispersancy was found in case of A_3 due to presence of higher number of –NH groups.

2.5.7 Performance analysis of phosphosulphurized Mannich bases

The prepared compounds B_1, B_2 and B_3 were added to the lube oil samples and the oxidation stability as well as detergency/ dispersancy of all samples under evaluation were determined and compared with lube oil sample without any additives.

2.5.7.1 As antioxidant

Mannich bases were treated with P_2S_5 to produce the additives B_1, B_2 and B_3. The prepared additives were added to the base oil and subjected to severe oxidation conditions using the Indiana test method discussed in experimental section. The oxidation stability is expressed in terms of change in total acid number (ΔT.A.N) and increase in kinematic viscosity ratio (v/v_0) and compared with the additive free lube oil. Results are given in **figures 2.5.9** and **2.5.10** which indicate the followings:

With increasing the number of –NH groups, the oxidation stability increases and therefore B_3 gave better results than others. In comparison to Mannich bases, phosphosulphurized Mannich bases gave somewhat better results. It is due to presence of phosphorous and sulphur. The sulphur and phosphorous compounds combine with metal to form sulphide and phosphide films that prevents the contact between metal surfaces and lube oil, and hence interfere with the catalytic action of metal on lube oil oxidation process.[24, 25]

2.5.7.2 As dispersant/detergent

The dispersancy values of phosphosulphurized Mannich bases are not very much different from those of dispersancy of Mannich bases. The values are given in **table 2.5.4**. The dispersancy capability mainly depends on the number of –NH groups present on the prepared additives. That is why B_3 has highest dispersancy capacity than B_2 and B_1.

2.5.8 Conclusions

This comparative study indicated that, addition of very small amount of prepared additives to lube oil enhances the efficiency as antioxidant and dispersant. It is also found that phosphosulphurized Mannich bases are more efficient as antioxidant than Mannich bases only. The performance of the additives increases with increasing number of –NH groups present in the additive. The prepared Mannich bases and phosphosulphurized Mannich bases additives have no any action on viscosity index and pour point of lube oil.

2.5.9 References

References are given in the bibliography section of chapter V of part II (Page No 192 - 194).

2.5.10 Tables and figures

Table 2.5.1 Physical properties of base oil

Density (g cm $^{-3}$) at 40 ^{o} C	0.84
Viscosity at 40 ^{o} C in c St	23.502
Viscosity at 100 ^{o} C in c St	3.98
Viscosity Index	85.12
Pour point (^{o} C)	– 6

Table 2.5.2 Theoretical and determined mean molecular weights of compounds A_1, A_2, A_3, B_1, B_2 and B_3

Prepared compounds	Theoretical	Determined
A_1	180	189
A_2	223	228
A_3	266	276
B_1	454	462
B_2	540	546
B_3	626	635

Table 2.5.3 Dispersancy of the base oil and its blends containing additives (A_1, A_2 and A_3) after different oxidation periods

Sample code	Dispersancy time (in hour)		
	24	48	72
Base oil only	42	40	35
Base oil +additive A_1	45	53	55.5
Base oil +additive A_2	63.6	66	68
Base oil +additive A_3	66.6	71	75.75

Table 2.5.4 Dispersancy of the base oil and its blends containing additives (B_1, B_2 and B_3) after different oxidation periods

Sample code	Dispersancy time (in hour)		
	24	48	72
Base oil only	42	40	35
Base oil +additive B_1	60	62	66
Base oil +additive B_2	63	71	74
Base oil +additive B_3	64	71	77

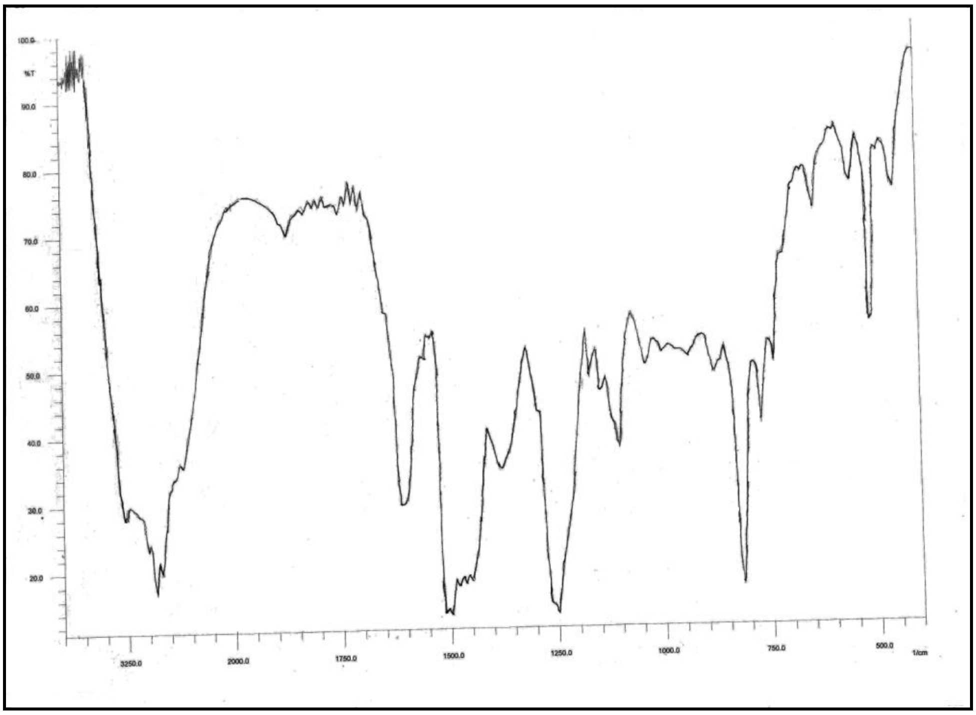


Figure 2.5.1 IR spectra of Mannich base A_3

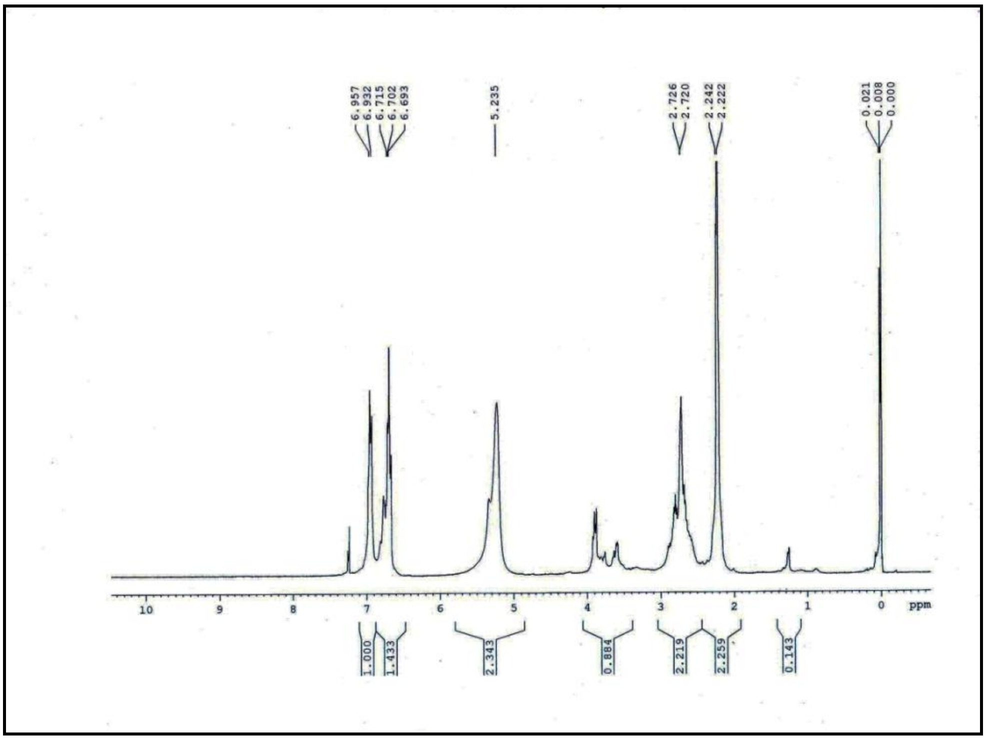


Figure 2.5.2 ^{1}H NMR spectra of Mannich base A_3

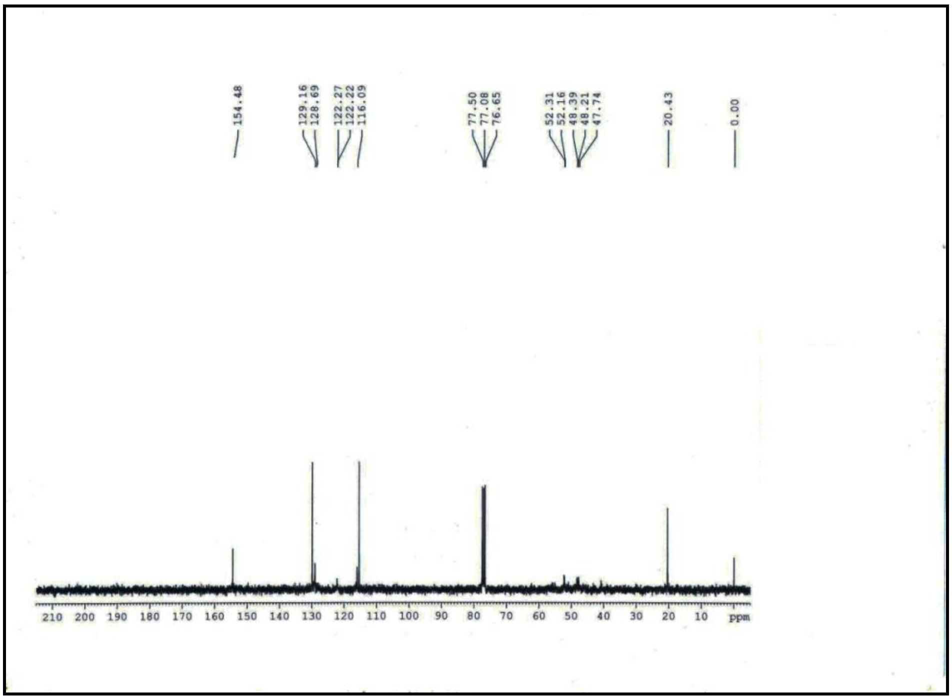


Figure 2.5.3 ^{13}C NMR spectra of Mannich base A_3

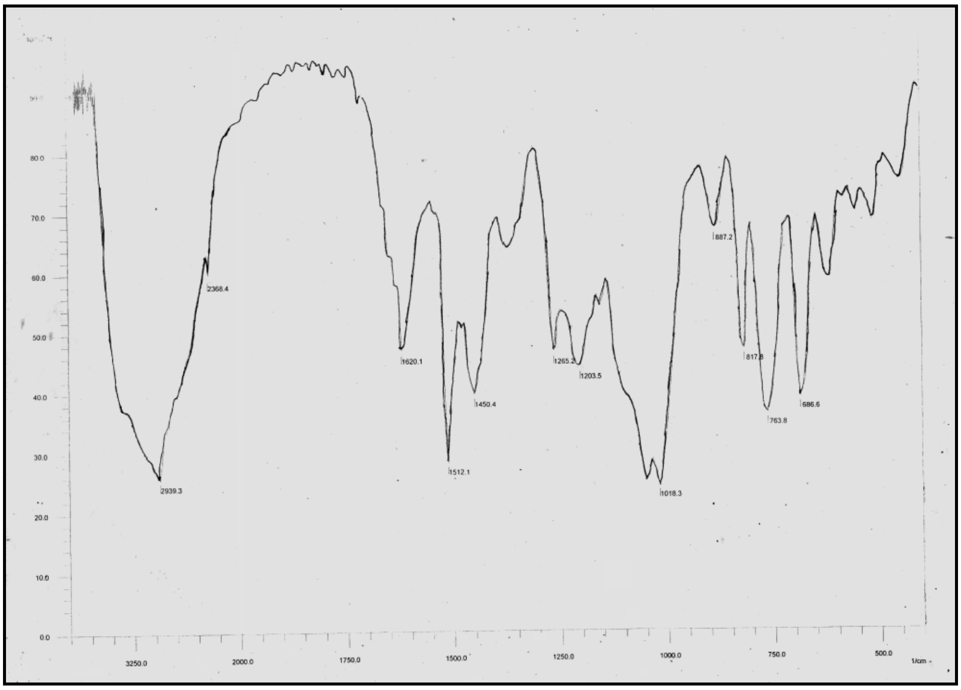


Figure 2.5.4 IR spectra of phosphosulphurized Mannich base B_1

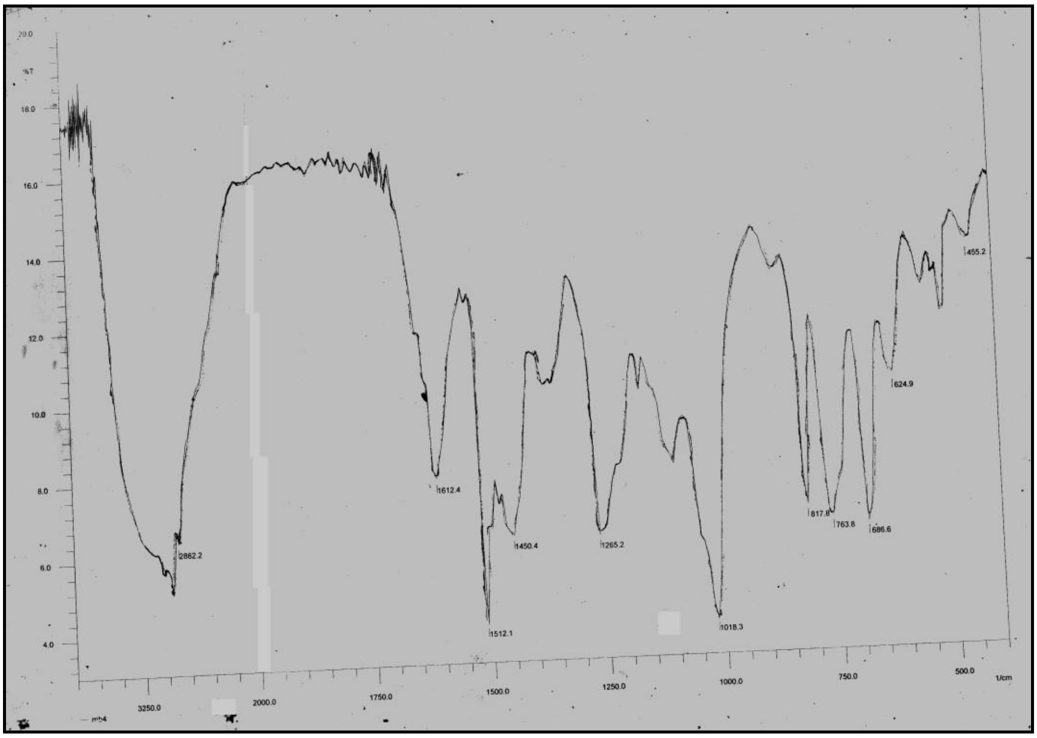


Figure 2.5.5 IR spectra of phosphosulphurized Mannich base B_2

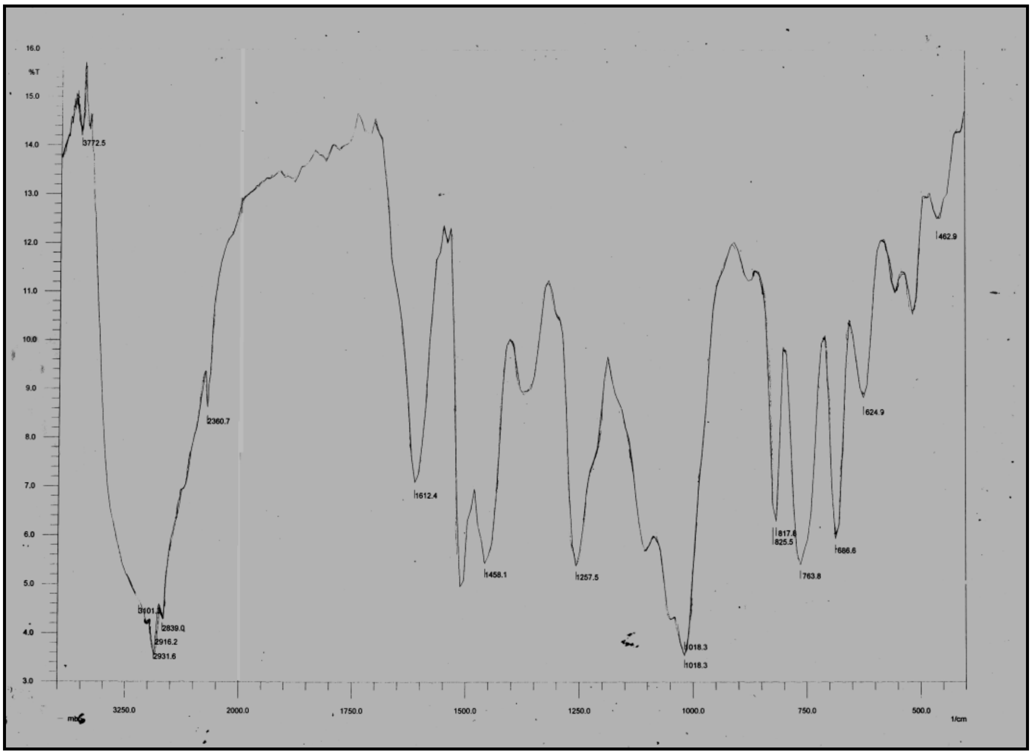


Figure 2.5.6 IR spectra of phosphosulphurized Mannich base B_3

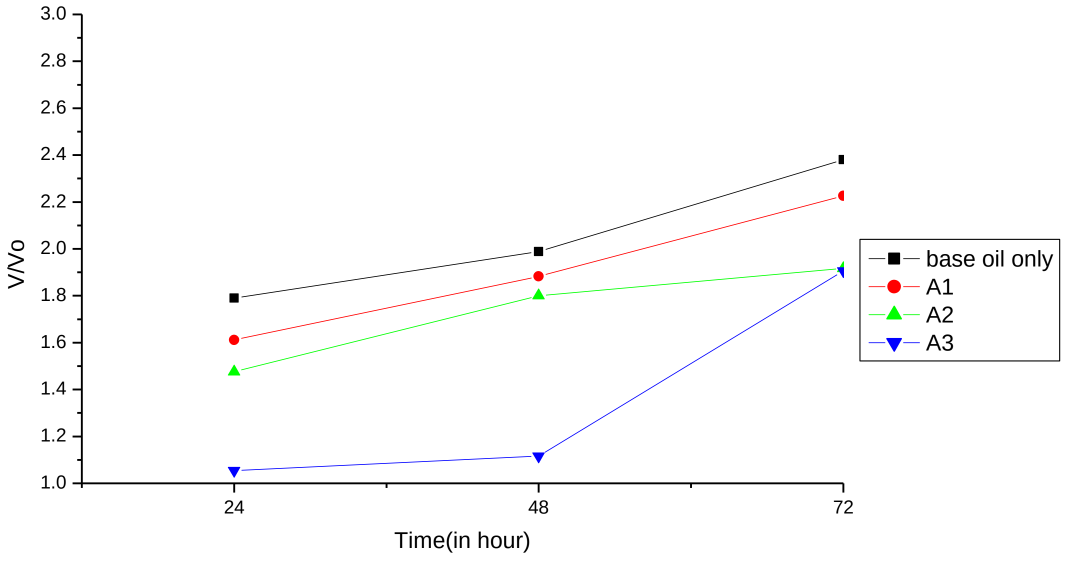


Figure 2.5.7 Variation of V/V_o with oxidation time of lube oil without and with Mannich bases additives A_1, A_2 and A_3

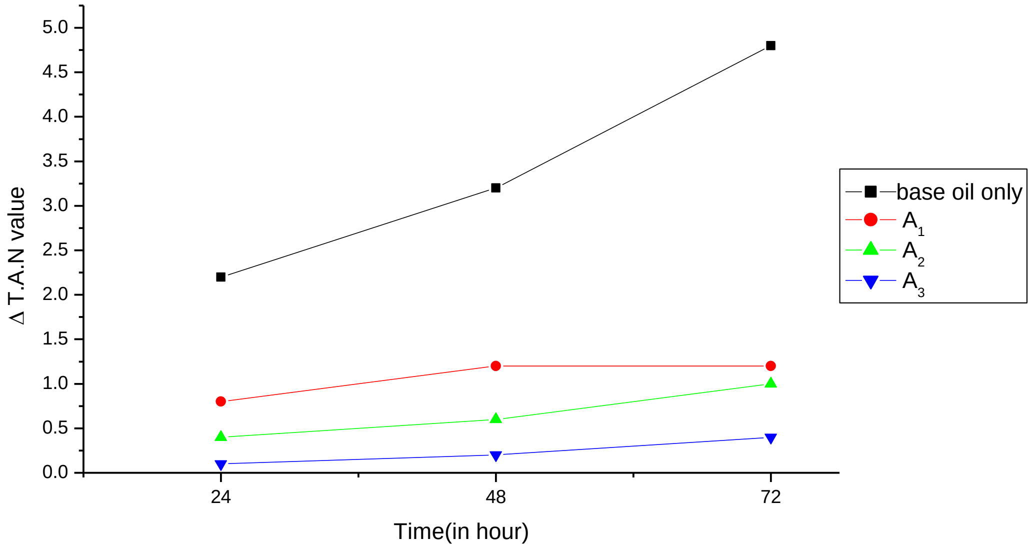


Figure 2.5.8 Variation of ΔT.A.N with oxidation time of lube oil without and with Mannich bases additives A_1, A_2 and A_3

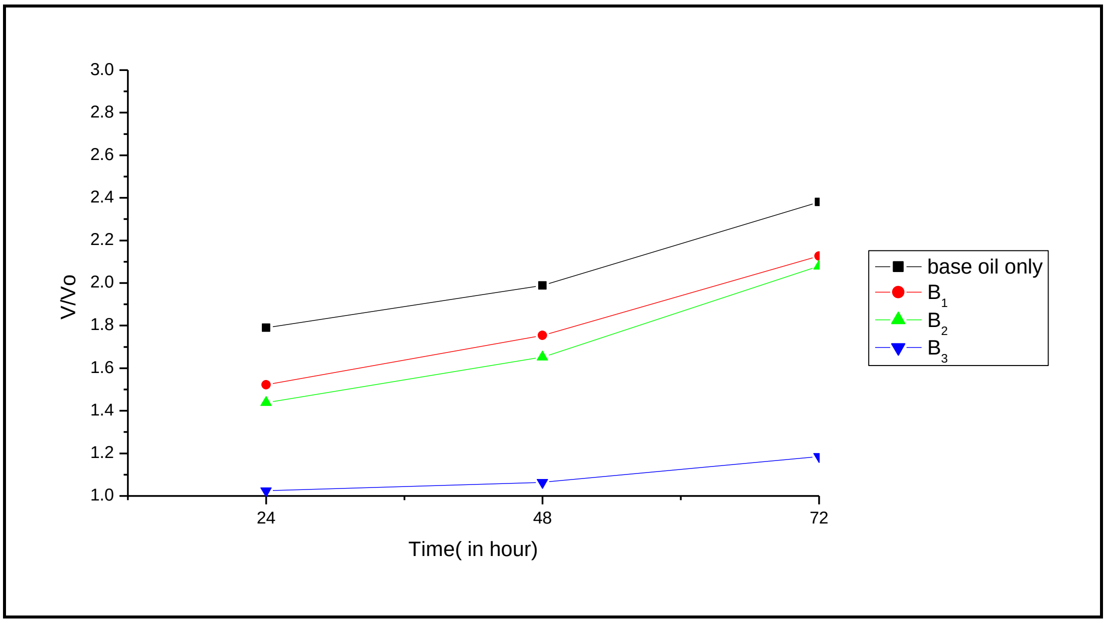


Figure 2.5.9 Variation of V/V$_o$ with oxidation time of lube oil without and with Phosphosulphurized Mannich bases additives B$_1$, B$_2$ and B$_3$

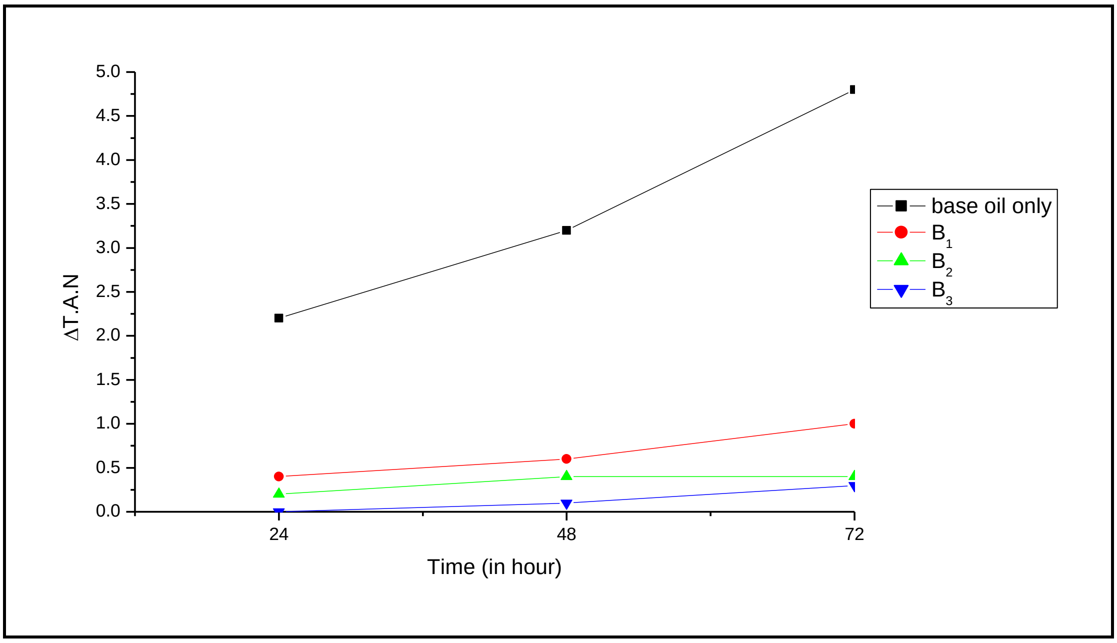


Figure 2.5.10 Variation of ΔT.A.N with oxidation time of lube oil without and with phosphosulphurized Mannich bases additives B$_1$, B$_2$ and B$_3$